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Investigating the influence of vehicular traffic on a major trunk road on rural air quality

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Signature……..

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Abstract

Traffic population in the UK has grown by 27% in 2002 and predicted to continue to an estimated 38% in 2016 and up to 60% by 2031. This means vehicular emissions from road transport may account for higher proportion of total emissions of pollutants resulting in air pollution with its attendant consequences. Although poor air quality concerns has often been linked to urban areas, many rural areas apparently have locations where air quality objectives may be threatened especially in the wake of increasing vehicular population. Thus, this elicits the necessity to investigate the relationship between vehicular emissions and air quality.

This study investigated the influence of vehicular traffic on a major trunk road on rural air quality through continuous measurements of nitrogen dioxide, sulphur dioxide and hydrocarbon between June 2008 and April 2010 along a major trunk road in a catalogued rural environment in the UK. Collection and analysis of pollutants was by Dräger short-term tubes and Dräger passive diffusion tube techniques. Throughout the sampling period, concentrations of sulphur dioxide were not detected using the short-term tube technique but were detected by the passive diffusion tubes. The study found that variations in mean concentrations of the pollutants were synonymous with traffic frequency and were influenced by meteorological conditions especially wind speed, temperature and relative humidity. Results observed concentration decline trend with increasing distance and showed maximum concentrations during winter, mainly in areas of close proximity to anthropogenic source, and minimum in summer. Values between winter year 1 and winter year 2 monitoring campaigns showed significant difference ($P<0.05$ and R=0.91) as was in summer year 1 and year 2 ($P<0.05$ and R=0.94), spring year 1 and year 2 ($P<0.05$ and R=0.84) and autumn year 1 and year 2 ($P<0.05$ and R=0.79). When compared with the guidance limits, NO_2

showed exceededance at roadside and 50 m, and at some sample sites, up to 100 m from the road. Conversely, SO_2 did not show any exceedance but statistical analyses was mostly significant between concentrations and distance at $p \leq 0.05$, suggesting the variability of pollutants, as well as the influence of distance on their temporal and spatial distribution. Results also show that pollutants correlated very well with daily traffic population with strong positive r^2 and *R*-values.

Similarly, the study considered the application of hazel leave (*Corylus avellana*) and ryegrass (*Lolium perenne*) vegetation samples in monitoring rural air quality. Both samples were collected in different seasons and distances (5m, 50m, and 100m) from the A49 trunk road at four rural sites characterised with diverse traffic densities and anthropogenic activities. The aim was to determine the elemental content and trends within the samples and to investigate the influence of distance from the road, height from ground level, and sampling season on the elemental levels. The levels of Al, As, Ba, Ca, Si, Mg, S, Cd, Cr, Na, Ni, Sb, Se, Sn, Mo, Mn, C, K, P, Cl, Ti, Fe, Zn, and Pb were determined using X-ray fluorescence (XRF), inductively coupled plasma-mass spectrometer (ICP-MS), and Scanning Electron Microscopy-Energy Dispersive X-ray spectrometer (SEM-EDX). Results show that despite the traffic differentials between the sampling sites, the pollution level of heavy metals were generally low in all sampling site and concentrations of Cr, Cu, Ni, Pb, and Ti exhibited inverse relationship with distance, decreasing in levels with increasing distance from the trunk road. Although root uptake from the soil is a potential source of heavy metals, geochemistry research of the study area did not show any evidence that proves any major heavy metals deposit concerns in the soil. It is therefore possible that heavy metal emissions were deposited in a form that was not readily available for root uptake, thereby narrowing the presence of heavy metal pollutants to other potential

sources. However, this study found high level of heavy metals at the roadside measurements in the order of Zn (0.703 ppm) > Ti (0.346 ppm) > Cr (0.111 ppm) > Cu (0.106 ppm) > Pb (0.026 ppm) > Ni (0.025 ppm). They were found in different magnitudes higher than their respective levels at 50 and 100 m from the trunk road and therefore tend to support traffic origin.

Findings from this study show that heavy metals exhibited different degree of correlation between individual elements, ranging from very strong positive to weak, as well as negative correlations. Statistical analyses show that the elements predominantly exhibited statistically significant differences between elements and between distances from the road. Overall, findings from this study demonstrate that both vegetation species prove to be successfully useful in determining the pollution status and trends of traffic-related heavy metals.

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Dedication

In loving memories of Deaconess Elizabeth and Master Desmond Obara,
I dedicate this project to God Almighty and to my wonderful family.

Chapter One

Introduction

1.0 Introduction

Roads are often the nearest vehicle-related source of pollution to natural areas and emissions from vehicular road traffic have been found to contribute a significant proportion to the total pollution emissions in the UK (Dore *et al*., 2008), being generated as a result of fossil fuel combustion or emitted by catalytic converters (Sutton *et al*., 2000). Several studies have consistently reported elevated levels of vehicle-related air pollutants near busy roads and highways, with concentrations decreasing with increasing distance from the road. Traffic-related emissions are known major source of air pollution especially in urban environments, raising air quality concerns in urban areas. This makes monitoring of traffic-associated pollutants an important step in understanding their effects on air quality.

However, it is seemingly evident that many rural areas have locations where air quality objectives may be at risk by the steady increase of vehicles in use on the trunk roads. The vehicular growth rate for all motor vehicles is estimated to rise by about 5% against 1-2% growth rate of global population (Fenger, 1999) with the projection that the world number of cars will rise to one billion by 2020 and expected to stabilize at nine or ten billion between 2030 and 2050. As at 2002, an estimated 26 million cars drove a total distance of about 540 billion km per year in the UK and this was predicted to rise to about 653 billion km by 2010 (Colls, 2002). It is for this reason that pollution generated by motor vehicles is greater than any other singular anthropogenic source and therefore may be of great influence to air quality. This has raised the awareness of traffic as a major diffuse metal emission source and accentuates the need for detailed information regarding various traffic-related sources and how they are emitted and where they are dispersed or deposited.

In the UK, more than fifty per cent of the local authorities have areas of poor air quality, the majority of which are traffic-related (Conlan, 2010). Poor air quality can cause poor health conditions and therefore pose a common challenge to the population. An annual estimated 50, 000 premature deaths in the UK have been because of poor air quality (Dearnley, 2010) and there are growing concerns that air pollution can pose more intractable challenges than anticipated. For this reason, several measures including regular vehicle inspection and maintenance, use of catalytic converters, use of unleaded petrol, and use of reduced sulphur content in petrol, amongst others have been introduced to curb air pollution.

1.1 Historical background of air quality in the UK

The major historic air pollution problem faced by both developed and rapidly developing nations has been high levels of smoke and sulphur dioxide coming predominantly from the burning of sulphur-containing fossil fuels used for both domestic and industrial purpose. The resultant effects of this practice periodically became very dangerous in many urban and industrial areas. A notable example is in the extreme-case scenario as recorded in the London smog disaster of 1952 (Kampa and Castanas, 2008) and 1961 (Harrison, 2006; Colls, 2002) which resulted from increased levels of particulates and sulphur dioxide. The mortality accentuated by exposure to the airborne pollutants from the incident, estimated at the time to be about 4000 but now believed to be about 12000 people (Bell and Davis, 2001).

The mortality incidence triggered widespread action involving a reduction from high to low levels of air pollution and subsequent introduction of legal restrictions on emissions; a move that culminated in the passage of the UK Clean Air Act of 1956 (Harrison, 2006). Revised and amended in some instances to strengthen the renewed

interest of cleaning up of the atmosphere, the Clean Air Act generally identified two major categories of air quality that are regulatory in function. Primary ambient air quality standards targeted human health protection, while secondary standards were to protect human welfare, including the environment and structure, from damage (Colls, 2002). The Clean Air Act and its amendments added air pollution damage to vegetation (an attempt aimed at dealing with any damaging effects of air pollutants to vegetation) as part of the criteria set and evaluated by the secondary National Ambient Air Quality (Tong *et al*., 2007). Despite these measures, emissions crept in from the expansion in vehicle usage; thus, attention drifted towards the importance and contributions of road transport emissions towards air quality. However, strengthening these regulations and improving other vehicular emission reduction strategies have been undermined by the rapid growth of vehicular population over the years.

To this end, local authorities were empowered by law to carry out air quality review of some key air pollutants generated from industrial activity and/or road transport (UK Department of Trade and Industry, 2000). The authorities are mandated to use these standards to establish emission control strategies especially in the urban environments as well as managing the risk exceeding air quality objectives (Longhurst *et al*., 2006) contributing significantly to the reduction of vehicle emissions rate for most pollutants (AQEG, 2004). This will require the control of air pollution through a combination of monitoring, modelling and emission control strategies (Williams, 2008).

1.2 Current Trends

Several efforts have been made over the years to reduce the impact of vehicular

emissions with options ranging from regular maintenance of vehicles, disposal of old vehicles, traffic management, improvement of public mass transport systems, upgrading of roads and traffic flow, to cleaner fuel formulations. For instance, by the end of 2002, about 70% of the passenger cars were already equipped with catalytic converters as a measure to reduce emissions of pollutants (Kassomenos *et al*., 2006). Some adopted strategies aimed at reducing emissions of pollutants include, but not limited to

- limiting vehicular traffic in certain days (applied in certain parts of the world);
- alternating circulation of even and odd number plates;
- encouraging "go on foot on Sundays" (Xia and Shao, 2005);
- encouraging the use of bicycle; and
- improving the transport systems where people are encouraged to travel by bus and train rather than by personal cars.

However, regardless of the various technical advances made in engine technology, exhaust-after-treatment and fuel composition, traffic emissions still remain a major source of pollution which is why, according to Ghenu *et al*. (2008), monitoring studies are necessary to follow the development in local air quality.

1.3 Scope of the study

This study will investigate the distribution and seasonal variations of air pollutants between 2008 and 2010 along the corridors of the A49 trunk road using different analytical methodologies such as bioindicators, e.g. Ryegrass (*Lolium perenne* Linnaeus) and Hazel leaf (*Corylus avellana*) and gas-monitoring device (Dräger tubes). Attention will be given to the elemental components of particulate deposits by examining their variations over time at various distances from the trunk road taking

into consideration the prevailing traffic and meteorological conditions.

1.4 Study aims and objectives

Application of different approaches in the assessment of vehicular influence on air quality near roads found elevated concentrations against the overall urban background level of air pollutants. The use of biomonitoring species (Lehndorff and Schwark, 2010; Ayrault *et al*., 2007 & Wolterbeek, 2002) and passive diffusion tubes (Laffray *et al*., 2010) have been employed to assess air quality status. The findings provided the basis for the assumption that air quality challenges are mainly urban-indexed. This study aims at investigating differences in main pollutant concentrations depending on the distance from the trunk road and assessment of seasonality impact on concentrations in a catalogued rural environment. Therefore, the following objectives were set out to achieve the study aims:

- To determine the rural concentrations of NO_2, SO_2, HC using short-term and passive diffusion tubes with respect to different distances from the A49 trunk road;
- To examine the relationship between traffic frequency and concentrations of measured pollutants;
- To assess the influence of meteorological parameters on the measured gaseous pollutants;
- To investigate the heavy metal pollution levels of hazel leaf (*Corylus avellana*) and ryegrass (*Lolium perenne*) along A49 trunk road in order
- To determine if elemental profiling of particulate deposits vary with height, and with distance from the emission source, i.e. the roadside.

1.5 Significance of the study

Due to heavy reliance on automobiles for transportation, it is anticipated that vehicular traffic frequency on roads may influence emissions that, at certain levels, could considerably reduce air quality. Therefore the principal prerequisite is to have a better understanding of the spatial and temporal distribution of air pollutants (Lindley and Walsh, 2005) as to know what to look for, when, where, how and why. Such understanding can be achieved by performing air quality measurements which, according to (Zamboni *et al*., 2009), will compare pollutant levels with the public health limits. The overall significance of this study is to advance the knowledge base of vehicular traffic influence on concentration of pollutants so that exposure levels, especially of people living near trunk roads, and their possible health and environmental impacts could be considered by local authorities in decision making and possibly engage in ways of reducing transport emissions. Therefore, findings from this study will provide a valuable reference or baseline for the future for policy makers leading to recommendations for environmental organizations and enforcers.

1.6 Research design

This research requires monthly sampling of air, particulate, vegetation, as well as traffic surveys be conducted throughout the season in the manner that will show true representativeness of the samples.

In Chapter One, the general introduction including the historical and background overview of air quality in UK as well as the current trends in reduction of vehicular emissions will be presented. Chapter Two will critically review relevant literature and methodologies employed in previous traffic emission studies. The experimental design and methodology used for this study including scanning electron microscopy

(SEM), X-Ray Fluorescence (XRF), and inductively coupled plasma (ICP) will be presented in Chapter Three. It will also present the description of the study (sampling) area, sample collection techniques and their laboratory preparations. Chapter Four will examine the laboratory results as well as results from the field surveys while Chapter Five will be for the interpretation of results obtained from both field data and laboratory experiments. Chapter Six will present the conclusion of findings and the overall significance of this study as well as the recommendations for future work.

1.7 Conclusion

This chapter examined the concept of emissions of pollutants and their influence on air quality. The chapter highlighted that the contribution of motor vehicles to air quality in the urban areas extended from as far back as the industrialization era. Increase in the population of vehicular usage was identified as the main singular source of poor air quality and accentuates why traffic contributions has become a very important issue nowadays. In the wake of the growing health and environmental concerns, regulatory measures and standards aimed at minimizing the risk of exceeding air quality standards have been introduced.

Chapter Two

Literature review

2.0 Introduction

As stated in the previous chapter, motor vehicle is an important source of emissions and the increasing vehicular usage is considered as main threat to air quality. This has heightened a paradigm shift of attention from industrial and domestic contributions, to the role of road transport in air pollution. This chapter presents a review of literature related to road transport emissions and air monitoring studies.

2.1 Trunk roads and air quality assessment

One of the fastest growing modes of transportation is the use of trunk roads (Demirel *et al*., 2008). Trunk roads and other similar major roads are routes of national importance that link important population centres and destinations (Azimi *et al*., 2005 & Truscott *et al*., 2005). They connect urban, suburban, and rural areas (Fang *et al*., 2007), serve as a significant conduit between larger towns and cities as well as residential and commercial locations, and as such, have traffic of a different scale and variety than smaller local road systems. Trunk roads include a whole suite of road types ranging from small country lanes through to motorways and in some parts of the world, 7-10 lane highways and are characterized by high traffic density. While it provides social and economic importance for the society, road transport can cause undesirable impacts such as traffic air pollution (Int Panis *et al*., 2011).

High traffic density exemplifies increase in traffic population and parallels increase in emissions that potentially contributes to poor air quality, and therefore has raised the awareness of air quality status. Because health and quality of life can be affected by the quality of breathed air, it is important to monitor air quality to understand if there are risks of exceedance of the guidance level and how such risks can be effectively managed. Assessing air quality status involves regular monitoring survey to ascertain

concentration levels of pollutants. Oxley *et al*. (2009) studied the road and urban transport modelling of air quality limits and acknowledged that monitoring air quality can provide a representation of pollutant concentrations at a relatively small number of points. Previous study (Sokhi *et al*., 2008) near a heavy trafficked road found that vehicular emissions could be underestimated and suggest that both exhaust and non-exhaust sources of emissions need to be quantified. This position lends credence to the need for regular air quality assessment.

2.1.1 Use of biomonitors

The use of biomonitoring techniques have been applied in monitoring pollution with the growing aerial deposition of pollutants to leaves in UK green spaces in urban and rural roadside environment. While many studies have used different plant species to monitor pollution (Real *et al*., 2003), it is important to note that only the plant species that can accumulate toxic compounds without any deleterious effects are often used for quantitative monitoring systems.

Wolterbeek (2002) defined biomonitoring as the use of bio-organisms or materials to obtain quantitative information on certain characteristics of the biosphere. Because continuous monitoring of air quality at high spatial resolution has proved to be very expensive, there has been a renewed interest in the use of plants as atmospheric pollution monitoring tools. Biomonitoring technique has been proven easier and cheaper than physical-chemical monitoring techniques as a means of assessing trace elemental concentrations in aerosols and depositions. It is also an important complementary technique to determine the biological effect on plants exposed to target pollutants (De Temmerman *et al*., 2007). Their use provides a cost and time-effective alternative to expensive technical equipment in measuring the concentrations

of specific substances in the bio-monitor tissue (Wolterbeek, 2002), and as such, this application is widely found in environmental research.

Different plant species including mosses (Harmens *et al*., 2007), ryegrass cultures (De Temmerman *et al*., 2007; Rey-Asensio and Carballeira, 2007 & Franzaring *et al*., 2006), purple moor grass (Laffray *et al*., 2010), lichen and moss (Adamo, *et al*., 2008), have been useful as biomonitors. The basic criteria for selecting these plant species as biomonitors include their wide geographical distributions, easy to sample and identification characteristics.

Plant leaf is one of the pathways through which atmospheric pollutants gain access to the plant. This is because the plant leaf, depending on its morphology, can easily trap significant quantity of pollutants released by motor vehicles. The pressure from increased traffic population has resulted in the exposure of urban trees to heavy metal pollution (Li *et al*., 2007) therefore, it is expected that leaf in urban environment will be susceptible to heavy metal pollution. Seeing that major physiological processes in plants are concentrated in the leaf, plant leaf is the most sensitive part of the plant affected by air pollutants (Renjini and Janrdhanan, 1989) and have been primarily recognized as accumulative biomonitors of trace metal pollution (WHO, 2000). This has attained wider application in atmospheric pollution studies. Monaci *et al*. (2000) monitored airbone metals in an urban environment using biomonitors and found new tracers of vehicle emission in place of lead. Howsam *et al*. (2000) studied hydrocarbons associated with hazel leaves during the growing season and found that the uptake of hydrocarbons from air is dependent on the air concentrations. They found that the increase in maximum concentrations of hydrocarbon corresponded to the increase in concentrations of hydrocarbon in air. Tomašević *et al*. (2005) used

Turkish hazel plant leave (*Corylus colurna* L.) to monitor urban trace metal pollution by analysing the particle deposits on the leaf sample during the vegetative phase. Results from that study suggested that hazel leave samples are good biomonitors. Similarly, Klumpp *et al*. (2002) used Italian ryegrass to assess urban air quality by determining the accumulation of toxic substances in leaves and detected heavy metal contamination in leaves in traffic-exposed sample sites.

Naveed *et al*. (2010) used roadside leaves (*Dalbergia sissoo* Roxb, *Prosopis juliflora* L. and *Eucalyptus* spp.) from urban, suburban, industrial, roadside and rural environments to investigate traffic related lead concentration in plants and obtained the highest lead concentration in *Dalbergia* plant sample collected from industrial site and the lowest in *Eucalyptus* in the rural site. Pourkhabbaz *et al*. (2010) studied the influence of traffic pollution on leaves by comparing urban and rural concentrations of heavy metal in air using plain trees (*Plantanus orientalis* L.) and found higher concentrations of heavy metals in the sample collected in the urban environment.

While these approaches have been able to provide significant information about the application of those plant species as important bioindicators, it will be interesting to investigate the usability of different plant species in a rural environment. Therefore, one of the objectives of this research is to employ the biomonitoring technique to characterize leaf samples of hazel plant (*Corylus avellana*) and ryegrass (*Lolium spp*.) collected during their growing phase in a rural environment.

Hazel plants are widely distributed in Britain. They are deciduous and predominantly in their growing phase during spring and summer. Where they are found during autumn or winter, their leaves (**Plate 2.1**) are usually scanty and yellow, thus their analyses during those seasons may not give reliable results. With this in mind, only

the analyses from spring and summer will be presented in this study. The leaf surface morphology is an important factor in determining uptake and retention of atmospheric pollutants (Howsam *et al*., 2000). Hazel leaves are characterized with physical characteristics including round-shape leaves measuring about 10 cm across and pointed at the end, doubly jagged leaf edges, and most importantly, hairy leaves. The hairiness of the leaf gives a rough texture that plays a significant role in the scavenging and retention of atmospheric particles. This is made possible by using a greater surface area together with the leaf hairiness and a layer of relatively stagnant air, called the boundary layer, at the leaf surface, thereby enhancing retention of impacted particles (Bakker *et al*., 2000). Similarly, ryegrass (**Plate 2.2**) are widely distributed and easily identified in Britain. They are common along the study area; therefore, it was readily available for sampling and analyses as a bioindicator for this study.

Plate 2.1: Hazel leaves (*Corylus avellana*)
(Source: Rook, 2002)

Plate 2.2: Ryegrass (*Lolium perenne*)

Source: Seedland (www.ryegrasses.com): accessed 10th May, 2011

2.1.2 Use of gas detection devices

Gas detection device is a useful tool in routine urban air quality surveys (Stevenson *et al*., 2001), spatial variability studies (Soares daSilva *et al*., 2006), epidemiological studies (Sunyer *et al*., 2006), and in targeted personal exposure studies (Chao and Law, 2000) in the UK. The basic principle is to measure either the instantaneous (short term or active) concentrations of the analyte at a particular time, or passive, the time-weighted average (TWA) concentrations. The device, usually packed with an inert adsorbent coated with reagents, changes color in the presence of a specific pollutant. It measures the concentration of target pollutants over a given time and has high correlation results as compared to continuous monitors (Lozano *et al*., 2009).

Diffusion (passive) sampler works on the principle of taking sample of gases at a controlled rate of molecular diffusion through the static air layer but does not involve active movement of air through the device. It measures the concentration of target pollutants over a given time. It is simple to use, low operating cost as it needs no

electricity or power source (Seethapathy *et al*., 2008 & Zhu *et al*., 2008), and has high correlation results as compared to continuous monitors (Lozano *et al*., 2009). Passive samplers are widely deployed in various environmental assessment studies. Vardoulakis *et al.* (2002) sampled a wide range of traffic-related atmospheric pollutants at various heights and distances from the kerb in two street canyons in France and found strong spatial concentration gradients in both sampling sites. In a related study, Beckerman *et al*. (2008) measured NO_2 and NO_x at various distance from the expressway using passive samplers for a four days exposure period. They obtained similar distance decay gradients with the monitored pollutants whereas Vardoulakis *et al* (2009) compared the concentrations of NO_2 and NO_x in three roadside locations using sets of passive sampler tubes exposed during a 4-week periods in an urban environment and found the sampling and analytical precision of the hand-held device satisfactory for NO_2 measurements.

The short-term tube device is similar to the passive in terms of detecting the presence of target pollutants, but within a short-time interval. The advantages are also similar to the passive sampler in having no need for power sources and requiring little or no training with the overall practical benefits of simple operational requirements and cost effectiveness. It measures the instantaneous concentration of target pollutants at a particular time. Vardoulakis *et al*. (2002) sampled different traffic-related pollutants at various heights and distances from the emission source using the active sampling technique at one-hour intervals and identified strong spatial concentration gradients. However, this study will combine both active and passive samplers to investigate variability and distance decay gradients of target pollutants in a rural environment.

2.2 Reviewing and assessing air quality

Reviewing and assessing air quality, especially, of a local authority requires three main stages. According to Ing *et al*. (2001), the first stage involves identifying, and gathering data from all the emissions sources including transport, industrial, other relevant sources of significant values and the background concentrations of the main pollutants. In a general sense, this stage does not mandate local authorities to carry out air quality monitoring but shows a demonstration of commitment that the local authorities have a thorough knowledge of the sources of pollutants of concern.

The data from the first stage provides an insight into areas of possible high occurrences of emissions. Therefore, the second stage involves selecting a number of areas with the likelihood of the highest occurrence of pollutants concentrations. Finally, the pollutants identified by the first and second stages, and their respective locations, triggers monitoring. This stage requires that the local authorities provide a detailed emissions inventory, validated dispersion models, and employ the use of quality and controlled continuous monitoring data (Longhurst and Elsom, 1997).

2.3 Air quality objectives

Although the control of air pollution is not a completely recent task, local authorities in the UK are required to regularly review and assess air quality, especially by comparing the ambient concentrations of pollutants considered as health and environmental threats. The reason for this is to determine the areas where air quality objectives are likely to be threatened and to develop action plans towards air quality improvement. Some of the pollutants for which the local authorities in the UK are responsible include particulate matter, sulphur dioxide, nitrogen dioxide, carbon monoxide, lead, benzene, 1, 3-butadiene (Vardoulakis *et al*., 2007 & Ing *et al*., 2001).

As a guide to protect health, the National Air Quality Strategy (NAQS) established health-based standards for these pollutants. The main objective of these standards was to reduce emissions by national action and at local level by empowering the local authorities to reach the set objectives within a set period (DETR, 2001 & Dpartment of Environment, 1997). **Table 2.1** shows the air quality objectives of the pollutants of major concern including NO_2, SO_2, PM and lead. Their emission, either singularly or in synergy with other elements, constitutes air pollution. Leksmono *et al*. (2006) were of the view that the air quality limits with the likelihood of being exceeded in the UK are NO_2 (annual and 1-h means), PM_{10} (annual and 24-h means) and SO_2 (15-min mean). In fact, exceedances of some pollutants (*e.g.* NO_2 and PM_{10}) have been reported in more than 200 local authorities in the UK (Vardoulakis *et al*., 2007) with over 95% designated traffic-related emissions (Longhurst *et al*., 2003).

Table 2.1: Current UK Air Quality Objectives

Pollutant	Concentration	Measured as	Target date
Lead	0.5 μgm^{-3}	Annual mean	31 December 2004
	0.25 μgm^{-3}	Annual mean	31 December 2008
Nitrogen Dioxide	200 μgm^{-3} not to be exceeded more than 18 times a year	1-hour mean	31 December 2005
	40 μgm^{-3}	Annual mean	31 December 2005
Sulphur Dioxide	350 μgm^{-3} not to be exceeded more than 24 times a year	1-hour mean	31 December 2004
	125 μgm^{-3} not to be exceeded more than 3 times a year	24-hour mean	31 December 2004
	266 μgm^{-3} not to be exceeded more than 35 times a year	15-minute mean	31 December 2005

Source: Defra (http://aqma.defra.gov.uk/objectives.php) - accessed on 5th July 2011.

2.4 Factors influencing traffic emission of pollutants

2.4.1 Car ownership and usage

A strong increase in traffic abundance has been reported by several studies (*e.g*. Demirel *et al*., 2008 & Schnitzhofer *et al*., 2008) and by the year 2000, the world motor population growth had reached 700 million (Ghose *et al*., 2004). However, the current population of automobiles has been estimation to be over 850 million (Mitchel *et al*., 2010). The population of motor vehicles in Beijing had exceeded 3.1 million by the end of 2007 (Beijing Traffic Management Bureau, 2008) and a recent study (Uherek *et al*., 2010) reported that the car fleet in the United States grew from 140, 000 to over 20 million vehicles in 20 years. This trend, according to Chen *et al*. (2009), is evidenced by severe traffic jams and slow speeds, which can significantly contribute to the degeneration of air quality. Similarly in the UK (Scotland), the number of vehicles in 1992 (1.679 million) has reportedly grown to 2.3 million in 2002 representing an increase of 27% (Department of Transport, 2003), a trend that has been predicted to continue with an estimated UK traffic growth of 38% from 1996 to 2016 and 60% from 1996-2031 (Department of Transport, 1997).

Chen *et al*. (2008) established a relationship between the growing vehicle population, road traffic congestion, and the resultant emission and proportion of pollutants such as nitrogen oxides (NO_x, 45%), and PM_{10} (25%). They concluded that such association could greatly influence vehicle emissions and in turn contribute to poor air quality.

2.4.2 Vehicle and driving condition

Motor vehicle traffic is a major source of air pollution in many urban areas, contributing between 57-75% of total emissions (WHO, 2006). The influence of

driving speeds and traffic density contributes to vehicular emission rates (Broderick and Mamane, 2002). Owen (2005) found increased level of NO_x emissions with an increase in average speed and a comparison of the level of pollution from vehicles moving with high speed at about 120km/h or above or moving with constant and moderate speed, showed that the latter emitted less air pollutants. The rapid increase in the number of motor vehicles in use has resulted in traffic density and this is usually associated with vehicle idling, deceleration, acceleration and cruising, resulting in worsening of air pollution (Chen *et al*., 2009 & Chan and Chung, 2003). This probably explains why road network improvements have become a viable option to maintaining steady speed of road traffic (Stranger *et al*., 2008).

Apart from driving conditions, vehicle conditions such as vehicle model, engine size, annual mileage, vehicle maintenance, age and exhaust control equipment (Bachman *et al*., 2000), vehicle engine combustion technology, exhaust after-treatment devices, and type of fuel used (Soylu, 2007) also play significant part in vehicular emissions. This has attracted several measures and strategies including fuel quality improvements and the introduction of clean fuel vehicle technology, aimed at regulating emission control of both in-use and new vehicles (Hao *et al*., 2006). **Table 2.2** shows the emission volumes at different driving modes for different fuels.

Table 2.2: Exhaust gas concentrations from different driving modes

Fuel and pollutants	Emissions (ppm by volume in the exhaust)			
Petrol	*Idling*	*Accelerating*	*Cruising*	*Decelerating*
HC	5300	1600	1000	10000
NOx	30	1020	650	20
Diesel				
HC	400	200	100	300
NOx	60	350	240	30

Source: Colls (2002)

2.4.3 Meteorological parameters

Poorly defined meteorological information is capable of producing misleading results with consequent inaccurate interpretations (Seaman, 2003). A typical example is the variation in concentrations observed during field sampling of pollutants which was attributed to not taking adequate cognizance of meteorological factors, and therefore capable of giving unreliable results (Ainslie *et al*., 2008). Air quality is not solely affected by emissions of pollutants alone but in synergy with different meteorological factors (Gupta *et al*., 2008). It is also a well-known fact that surface concentrations of air pollutants in European countries are largely dependent on meteorological fluxes (Rost *et al*., 2009 & Solberg *et al*., 2008). In the light of this, Guus and Jan (2009) highlighted the importance of knowing the extent to which meteorological fluctuations can influence the concentrations and consequently affect the EU limit values in future years. A typical example is in the findings that high NO_2 levels from

traffic emissions in busy streets are dependent on meteorological conditions (Koroneous & Nanaki, 2007). Thus, meteorology is of significant importance in air quality studies influencing the severity of air pollution events (Hu *et al*., 2010 & DeGaetano & Doherty, 2004).

2.4.4 Land topography

Landscape topography of a particular location plays a key role in air pollution studies. The topography of a place is capable of forming a partially enclosed volume in that can greatly affect atmospheric mixing and transport (Beauchamp *et al*., 2004). Radojević and Bashkin (2006) posited that the occurrence of air pollution episodes is contingent on the prevailing topography of the study area. They argued that the prevailing topography could create a low-lying inversion that can restrict pollution dispersion. There is therefore the possibility that pollution can be trapped between mountains (Beauchamp *et al*., 2004), hills (Kim *et al*., 2001) and the inversion layer, affecting mean-flow advection known as an effective process of pollutant transport. Wotawa *et al*. (2000) demonstrated topographical and meteorological influences on the concentrations of air pollutants with the same emission source strength and found concentrations of NOx in the valley nine times higher than in flat terrain.

2.5 Sources of emissions in the UK

The emission source categories in the UK include road transport, industrial, commercial and domestic, and fugitive or uncontrolled sources (Defra, 2009). The following sections consider details of the source categories.

2.5.1 Road transport source

The significance of road transport include door-to-door transportation (Soylu, 2007), provision of mobility, facilitating industry and trade (Koroneos and Nanaki, 2007). Road transport makes a very important contribution to the economy and cultural exchange between societies (White Paper, 2001). Road transport source category comprises of narrow congested streets with residential properties close to the kerb; busy street where people may spend 1-hour or more close to traffic, roads with a high flow of buses and Heavy Goods Vehicles, and roads with significantly changed traffic flows (Defra, 2009).

Despite the socio-economic benefits of road transport, it is a key source to many air pollutants (Defra, 2007; Potera, 2004 & Colls, 2002) and therefore steady growth of the number of cars in the UK (Offer *et al*., 2011) may represent increase in traffic contribution to emissions of air pollutants. This is because road transport accounts for 63% of the total trips made, and an estimated 80% of total distance travelled in the UK in 2008 (DfT, 2009) and considered a serious threat to air quality and global warming (Colvile *et al*., 2001).

Road transport, considered as the main source of air pollution within the rural-dominated area of Shropshire (study area), is presumably the most pollutant source with the tendency of exceeding the air quality objectives. This is because traffic within this rural locality is growing faster than in most parts of the country, thus, presenting the potential of an exceedence of the air quality objectives of the study area. With the growth prediction of 15% from 2003 to 2015, traffic in rural areas is expected to grow more in parts of UK to around 22% between 2003 and 2025 (SLT, 2010).

The UK National Atmospheric Emissions Inventory reported that road traffic is the largest emission source of many health-related air pollutants (AEAT, 2004), contributing about 48000 tonnes per year of emissions into the atmosphere (APAT, 2005). This may explain why road transport is a key focus for national air quality strategy (Mitchell *et al*., 2005), with the main objective of developing policy, tasks and responsibilities for air quality management in the UK (DETR, 2000a).

Figure 2.1 compares the percentage contributions of emission of transport with industry source and shows that transport source dominated the emission contribution except for PM and SO_2. It is not surprising given that transport is almost completely fossil-fuel dependent and represents 67% of final energy consumption (European Commission, 2000a).

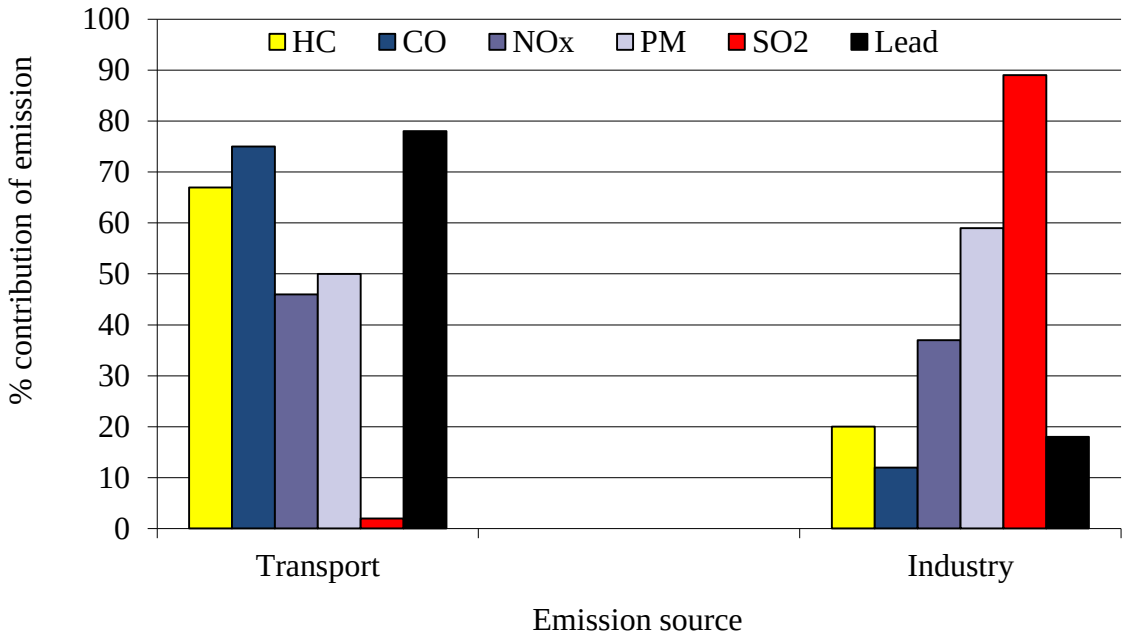

Figure 2.1: Emissions in UK (www.defra.gov.uk/environment/airquality) - accessed 5th July 2011

2.5.1.1 Road dust emissions

Road dust is described as loose materials (silt) lying in the irregularities of the road surface and characterized by the tendency of being entrained in the air by the turbulent air movement associated to the passage of a vehicle. Apeagyei *et al*. (2011) defined it as a complex mixture of particles originating from various natural and anthropogenic sources consisting of carcinogenic components and heavy metals from both exhaust and non-exhaust processes, as well as mold spores and pollen fragments along an urban-rural gradient. Road dust can subsequently become resuspended by passing vehicle-induced turbulence and shearing stress of the tires or wind (Kupiainen, 2007) and this process is believed to have contributed about 30% of the total PM_{10} in California (Colls, 2002). Apeagyei *et al*. (2011) studied the distribution of heavy metals in road dust in Massachusetts, USA, where they compared urban and rural road dusts. They found greater concentrations of some elemental components in urban road dust and therefore concluded that roadway dust is an important source of metals in localized resuspended particle matter. In the UK, Yin *et al*. (2010) investigated the source apportionment of fine particles at rural sites surrounded mainly by grass land, a very few residential houses and a local pub located 100m and 150m from the site respectively as well as few farm houses further away, with no centre of population within 1200m away. The nearest anthropogenic pollution source to the site is the A451 road in a distance of about 200m with a moderate to heavy traffic road and a light trafficked country road. Results from the study indicate that road dust and soil are important sources of particulate emissions. Major concerns about the temporal, spatial and size distributions of particulate pollution in rural areas of UK have also been raised and it is in view of this that the UK government initiated the campaign of monitoring particulates in locations, believed to be representative

enough, throughout the UK. Namdeo and Bell (2005) measured particulate concentrations in rural areas of UK by collecting sample deposits on filter cartridge. Results show higher road concentration of particles at both the urban kerbside site and the urban city centre especially during morning rush hours, suggesting the influence of high traffic flow. However, the rural concentration of fine particles was higher than that of the kerbside site, an indication that higher percentage of the particulate deposits are coarse particles and therefore of wind-dust, commercial and industrial origins, and less of resuspension due to traffic.

2.5.2 Industrial sources

There are several industrial processes located in the study area including coal fired power station, aluminium production, fertilizers, and incineration. Other industrial rural sources of pollution within the study area include large boilers and coal fired boilers, with SO_2 and PM_{10} as the main pollutants of concern respectively.

2.5.3 Other sources

Land use in the study area is predominantly for agriculture, amounting to 81% of the total land area. Movement of tractors and other farm machinery movements have the potentials of increasing the atmospheric burdens and subsequently contributing to the rural air quality status. Because most agricultural machineries are diesel engines, it is possible that they can generate particulate materials. This is consistent with Colls (2002) who noted that small diesel engines could emit about five g particles per litre of fuel and up to 12 g for heavy-duty engines. There is also a growing tendency that small levels of pollutants emitted from agricultural vehicles, dark smoke from bonfires and waste burning, and fugitive dust produced by agricultural processes may

affect localized areas. However, it is not clear if agricultural sources of pollutants are of such significance within the study area as to lead to a breach of any of the air quality objectives.

There is also significant contributions of erosion and resuspension of agricultural soils and other surface deposits transportable into great distances thereby resulting into loss of visibility and increase in atmospheric particle burden. This process, referred to as deflation, involves three key stages including suspension from the surface into the air, transport and finally, deposition. In addition, combustion (e.g. biomass combustion), and crushing of quarry products can generate different mixture of soot, sulphate, nitrates and hydrocarbons which ultimately have the potential of influencing atmospheric burden. This is because a significant proportion of particles released by these processes are fine enough to remain suspended in the air (Coll, 2002).

2.6 Air quality monitoring close to the road

Distance-from-highway studies have provided the means of assessing epidemiological importance of traffic-related air pollutants irrespective of the disparities in traffic flow, engine sizes, and fuels used (Hoek *et al*., 2002). Many air quality studies have recorded increased concentrations of air pollutants such as nitrogen oxides, particulate matter, and hydrocarbons near major roadways. Kittelson *et al*. (2004) measured emissions of aerosols in residential areas 10 -20 m away from the highway, sampling with different hand-held devices under different traffic conditions. Their results show increased aerosol with decrease in distance between sampling points to the roadway and lower concentrations in residential areas within 500-700m from the highway. Another highway study was by Gilbert *et al*. (2005, 2003) and Pleijel *et al*. (2004). They used passive diffusion samplers to measure the ambient nitrogen dioxide at

various distances (ranging from 0 to 1310m) and from a highway where daily traffic volume exceeded 100 000 vehicles and at a height of 2.5m from ground level. Their results show concentrations of nitrogen dioxide significantly corresponding with distance from the highway, declining beyond 200m from the roadway, noting that high-volume roadways influenced the spatial variability of NOx. The peculiarity of this trend is common in large cities influenced by different highway traffic volumes (Gilbert *et al*., 2005). McAdam *et al*. (2011) examined the distribution of traffic-related air pollutants in proximity to a major road with traffic volume of about 34 000 vehicles/day and measured the ambient concentration of SO_2, NO_2, and particulates ($PM_{2.5}$) at two different locations using different hand-held air samplers. Measurements took place at different distances from the road (10, 30, and 60m) and at different heights, (2.5 and 9 m above ground level). Their study did not find any significant differences, with respect to distance from road and height, for SO_2 level on the hourly average concentrations. However, at closer distance (10 m) from the road, the hourly average concentrations of NO_2 were 5.0-6.0 ppb higher than that at 30 m, which in turn are 3.0-4.0 higher than the 60 m distance from the road, suggesting either a traffic-dominant influence or meteorological dynamics. In Beckerman *et al*. (2008), the application of active and passive monitoring devices correlated nitrogen dioxide with other traffic pollutants near a major expressway. They found a distance decay trend with both devices with the concentrations of nitrogen dioxide decaying more rapidly in the first 50 m and attaining to background level around 400m from the road. That the concentrations at the 60 m location were higher than those of 30 m of the same transect suggests that sources other than vehicular emissions may have influenced $PM_{2.5}$ concentrations.

However, different distance-decay studies around busy roads reported different decay rates. Some found concentrations decline of up to 50% for particulates within 100-150 m from the road (Hitchings *et al*., 2000) and eventually merging into background levels at 150 m (Zhu *et al*., 2002a, b), others found decrease in total particle counts with distance levelling to background levels within 50m from the roadway (Tiitta *et al*., 2002).

2.6.1 Rural air quality monitoring

Rural monitoring sites are open country locations distanced from population centres, roads and industrial areas or locations without nearby emission sources such as industrial plants (DEFRA, 2004). To assess air quality on a national basis in UK, DEFRA employed several air measurement techniques including the use of short-term and passive (diffusion) tubes on representative background sites throughout UK with two key purposes. First was to generate a rural concentration field that will provide the basis for assessing the concentrations of metals in UK, especially at locations where monitoring is not carried out. The other purpose is to provide detailed information regarding the processes influencing concentrations and deposition of heavy metals, with the view of assessing any threat or risk arising from such deposition (Defra, 2010). They measured nitrogen dioxide, sulphur dioxide, and particulates, while heavy metal concentrations in air that were monitored include Arsenic, Cadmium, Chromium, Copper, Mercury, Nickel, Lead, Vanadium, Zinc, Aluminium, Titanium, Manganese, Iron, Cobalt, Molybdenum, Barium, etc. Results obtained show that the concentrations of Nitrogen Oxides was at highest levels at kerbside especially in areas characterized with poor dispersion, e.g. street canyons,

while the annual mean concentrations of NO_2 besides a busy road regularly exceeded the allowable limit of 40 μg/m^3.

Although aerosols and deposited dusts in rural areas comprise of some potentially toxic heavy metals, lead toxicity has become important due to its constant increase in the environment. It is in this light that Naveed *et al*. (2010) collected and compared results of leaves of three roadside plants at different locations of urban, suburban, industrial, roadside, and rural sites in both summer and winter seasons in order to determine the extent of lead (Pb) contamination in roadside plants. Results obtained show lead concentrations in the range of 61-429 μg/g with the lowest found at the rural site in all seasons.

2.7 Impacts of road transport emissions

Despite the advantages road transport provide, road transport system encourage changes in land use patterns, which in turn changes the travel demand, and ultimately influence the transportation system (Shaw and Xin, 2003). Road travel generates air pollutant emissions, greenhouse gas emissions, and noise (Brown & Affum, 2002) which can affect habitat, ecosystems, endangered species, and capable of fragmenting and replacing natural cover with impervious surfaces, as well as contributing to air quality status and global warming (USEPA, 2001). The impact of traffic-related pollutants on growth and development of plants along roadways has been extensively documented (Swanepoel *et al*., 2007 & Cape *et al*., 2004). The impacts may vary significantly with plant species (Ashenden *et al*., 2003) as commonly observed in forests close to motorways (Spangenberg *et al*., 2004 & Spangenberg and Kölling, 2004), or with the plant part such as leaf and stomata (Swanepoel *et al*., 2007 &

Larcher, 2003) for which their visual symptoms and biochemical effects have been recognized (Rakwal *et al*., 2003).

2.7.1 Ecological concerns of air pollutants

Numerous authors have studied the effects of traffic emissions on the surrounding ecosystems. Forman (2000) and Truscott *et al*. (2005) revealed that the ecological impacts of road traffic have significantly increased over the years. Bignal *et al*. (2008) studied the effects of air pollution from road transport on growth and physiology of six transplanted bryophyte species and found the strongest effects 50 to 100 m from the motorway. This is of a major concern especially in England where an estimated 5.4% of Sites of Special Scientific Interests (SSSIs) are within 200 m of a major road (Weigert, 2004). Many well-known air pollutants have common sources and demonstrate the tendency of interacting chemically and physically with greenhouse gases in the atmosphere and this interaction is capable of influencing different types of environmental impacts on local, regional and global scales (Bytnerowicz *et al*., 2007).

2.7.2 Public health concerns of air pollutants

The public health risks of traffic emissions have extensively received global attention especially as exposures to even relatively low concentrations of vehicle emissions can aggravate several health cases. In recent years, WHO (2003) reported an estimated number of deaths (about 6.4 million) resulting directly from air pollution each year. This seemingly exemplifies the growing global concern about atmospheric pollution. However, it has been noted that air pollutants from traffic and other sources are not

only a problem within the immediate vicinity of the emission source, but can travel long distances chemically reacting in the atmosphere and yielding secondary pollutants and impacting on rural areas, usually far from the original emission site (Oliveira *et al*., 2007).

Epidemiological studies have shown that air pollutants contribute to increased mortality, hospital admissions and damaging human health impacts (Brunekreef and Holdgate, 2002). Similarly, cancer, birth and developmental disorders, cardiovascular, mortality, asthma and other respiratory impacts have been associated to various air pollutants (McConnell *et al*., 2006). Furthermore, impaired health cases including, but not limited to, respiratory, cardiovascular, cancer, neurotoxological damage, birth defects, morbidity and mortality impacts have been linked to people living close to high traffic roadways (WHO, 2005a, b; Heinrich *et al*., 2005; Kim *et al*., 2004). There are evidences to show that people in residences and schools in close proximity to main roads are prone to exposure to high levels of vehicle pollutant emissions. Living near busy roads has elicited coughs, wheezes, runny nose, asthma, and allergic sensitisation, especially in children (Jansen, 2003, Nicolai *et al*., 2003). A study carried out in England and Wales suggested high risk of mortality from stroke when living near busy roads (Maheswaran and Elliot, 2003). Similarly, a Dutch cohort study demonstrates that living close to a freeway has been found to result in subjects having a significantly elevated risk of death resulting from cardio respiratory causes (Hoek *et al*., 2002), a development that has increased global concern and elicited epidemiological studies (Gupta *et al*., 2008).

2.8 Air Pollutants of interest

Researches have emphasised the importance of particulate matter, gaseous pollutants, organic pollutants, and heavy metals. Despite the apparent importance of these

pollutants including damaging environmental and health effects in the urban areas, their study in the rural areas is rare. Although primary airborne pollutants covered by European and other legislation include SO_2, NO_x (NO_2/NO), benzene, ozone, CO/CO_2, and Particulate Matter ($PM_{10}/_{2.5}$) (UK Environment Agency, 2004), the pollutants of interest for this study will be limited to particulate matter (PM), heavy metals, organic (*e.g.* hydrocarbon), nitrogen dioxide (NO_2) and sulphur dioxide (SO_2). These pollutants are either products of fuel or a product of their incomplete combustion or are involved in the combustion process (Koroneos and Nanaki, 2007) resulting in epidemiological concerns.

2.8.1 Particulate Matter

2.8.1.1 Sources

Particulate matter is the generic term used to describe the type of air pollutant that vary in size and composition, produced by a wide variety of natural and anthropogenic sources, and are made up of complex and varying mixtures of particles (Srimuruganandam and Shiva, 2011) suspended in the breathing air (Pöschl, 2005). In other words, particulate matter is a complex mixture of suspended particles whose features - physical, chemical and biological - determine its behaviour, environmental and health effects (EPA, 2004). Crustal materials, resuspended road dust, long range transport events (Vallius *et al*., 2005) and diesel-powered exhausts from vehicular traffic (Wåhlin *et al*., 2001) have all been established as the main sources of particulates. Road dust entrained into air by vehicles' movement (Patra *et al*., 2007) in addition to vehicular-induced turbulence affect the initial dispersion of pollutants from traffic emissions (Kalthoff *et al*., 2005) and ultimately generate PM. On a regional scale, Vardoulakis and Kassomenos (2008) summarised the principal causes

of the occurrence of particulate matter pollution in Europe to include strong traffic-related emission sources, poor local atmospheric dispersion conditions such as temperature inversions, wind, weather conditions that aid long-range dispersion of particles; and hard-to-control natural sources of coarse particles such as windblown dust, sea salt, etc. Oliveira *et al*. (2007) identified particulate atmospheric pollutants in most areas of Europe as mainly products of combustion from space heating, power generation or from motor vehicle traffic.

Considerable amount of particulate pollutants produced in livestock houses are traditionally discharged to the atmosphere through ventilation exhausts (Phillips *et al*., 1998 & Takai *et al*., 1998). This can compromise health and welfare of humans and animals, be a source of danger to plants and other organisms, and has the potential of causing vegetation stress and ecosystem alteration (Cambra-López *et al*., 2010; Grantz *et al*., 2003 & Pope *et al*., 2002). Other sources include construction, commercial and domestic combustion of solid fuels for heating (**Figure 2.2**).

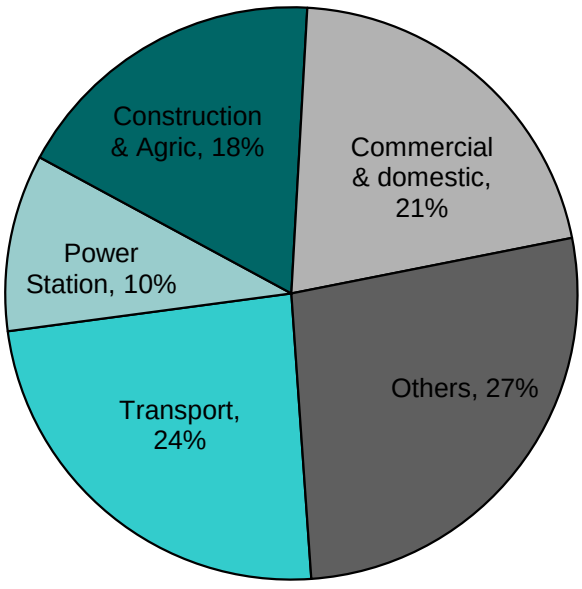

Figure 2.2: Sources of particulate matter

Source: Air Pollution (www.air-quality.org.uk) - accessed 5th July 2011.

2.8.1.2 Characteristics of Particulate Matter

In characterising particulate pollution, it is necessary to gain an insight into their mass concentration, size distributions, and their origins. Some authors (*e.g.* Ohlström *et al*., 2000) further categorised particulate matter into ultra-fine (those with aerodynamic diameter less than 0.1µm), fine (aerodynamic diameter less than 1µm), and coarse particles. The ultrafine and fine categories have been strongly characterised as more hazardous than the coarse particles. Although the composition of particulate matter varies since they can absorb and transport several pollutants, the main components of PM include metals, organic compounds, ions, reactive gases, and materials of biologic origin. Their metal content and other organic components are mainly responsible for their toxicity and health effects (Kampa and Castanas, 2008). In a separate study, Jonathan *et al*. (2004) classified those particles with aerodynamic diameter greater than 1µm as coarse particles, derived from abraded soil, road dust (such as brake and tyre dust), construction debris, or aggregation of smaller combustion particles.

2.8.1.3 Issues of concern for Particulate Matter

Because particulate matter is seen as the air pollutant with the most severe human health threat in the EU (European Environment Agency, 2005; WHO, 2003), it is expected that issues concerning particulates will attract significant attention for which Colls (2002) identified some issues of concern. Firstly, the long-term chronic health effects associated with very small particles of very low concentrations irrespective of

their composition. Secondly, the presence in those particles of heavy metals known to be very toxic; thirdly, the soiling characteristics of smoke particles on buildings and other surfaces; lastly, the light attenuation property of these particles and the subsequent reduction in visual range resulting in loss of amenity.

High concentrations of particulate matter (including aerosols and heavy metals) rely on their chemical composition to affect climate, enhance warming and generally have a cooling effect (Houghton *et al*., 2001). Atmospheric particulates are responsible for soiling buildings, visibility degradation, destroying ecosystems (Colls, 2002), thereby causing increased risk of traffic accidents. Elevated concentration of particulates also has the potential of affecting the earth's radiation balance and subsequently affecting weather and climate (Radojević and Bashkin, 2006). Particulate matter is one of the most important air pollutants that adversely influence human health in Europe (Koelemeijer *et al*., 2006) and its risk increases with increase in concentration (Koroneos and Nanaki, 2007). The human health impact of particulate matter in the last decade has been linked to respiratory illness (Elliot *et al*., 2007), increased mortality (Cambra-López *et al*., 2010), chronic respiratory effects (Pope, 2004) as well as aggravation of cardiovascular diseases, elevated disease and death frequency (Radojević and Bashkin, 2006). It is interesting to mention that the size of particulate matter play significant roles in the degree of their potency. For instance, childhood morbidity and mortality are associated to exposure to particles less than 10μm (Kappos *et al*., 2004).

2.8.2 Nitrogen Oxides (NO_x)

2.8.2.1 Sources

Nitrogen oxides are a group of very reactive gases containing different proportions of nitrogen and oxygen and include nitrogen dioxide, nitric acid, nitrates, and nitric oxides (Richards *et al*., 2006). In a new approach to deriving NO_2 from NO_x for air quality assessments of roads, Defra (2002) defined nitrogen oxides as the sum of nitric oxide (NO) and nitrogen dioxide (NO_2) emitted into the environment primarily as nitric oxide (NO) but undergo chemical transformation processes in the atmosphere to form nitrogen dioxide (NO_2).

Anthropogenic activities that involve burning of fuels are the principal sources of nitrogen oxides. Examples include motor vehicles, electric utilities, industrial, commercial, and residential sources (Pires *et al*., 2008; EPA 2003) with vehicular emissions alone constituting about 55% of the total anthropogenic emission of NO_x (EPA (2003). Pandey *et al*. (2008) concluded that nitrogen oxides occur when fuel burn at high temperatures thus correlates with the findings of Fang *et al*. (2007) who concluded that the principal sources of NO_x are fossil fuel combustion for industrial processes, electricity and automobile emissions and accounts for about 50% of such emissions.

Road transport accounts for more than a third of all NO_x emissions in the US (US Department of Transport, 2006) and more than half of NO_x emissions in the UK (AQEG, 2004). Some of NO_x emissions are emitted as nitric oxide (Carslaw and Beevers 2004) while about 10% are directly emitted as nitrogen dioxide (Cape *et al*., 2004). Vehicular emissions contribute an estimated 45% to total emissions (Dong *et al*., 2000) and there has been a strong association between the concentration of nitrogen dioxide in urban areas and traffic density (Da Silva *et al*., 2008), suggesting that traffic is the dominant source of the pollutant in most cities in Europe (Ghenu *et*

al., 2008). The dominant traffic source of nitrogen oxides pollution in the UK in 2001 is as shown in **Figure 2.3**.

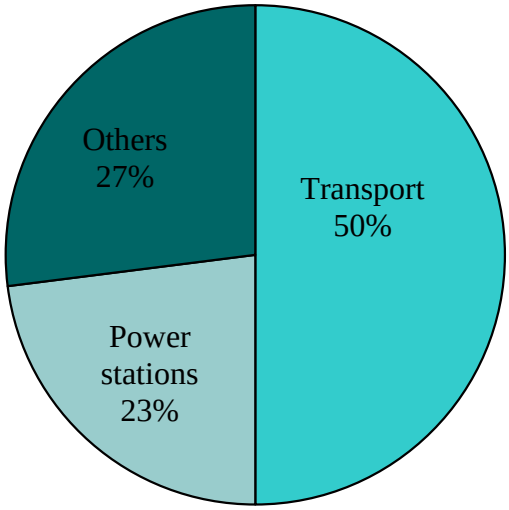

Figure 2.3: Sources of nitrogen dioxide

Source: Air Pollution (www.air-quality.org.uk) - accessed 5th July 2011.

2.8.2.2 Epidemiological and ecological concerns of Nitrogen Dioxide

Diverse negative effects on exposures to NO_x have generated various epidemiological studies. Nitrogen dioxide and NO are the components of NOx, and NO_2 known to be much more toxic than NO. However, the inhalation of nitrogen dioxide alone or in synergy with other pollutants could result in facilitating the airway response to inhaled allergens. This results in a possible aggravation of asthma in children (European Environment Agency, 2005 & Delfino *et al*., 2003), increased susceptibility to respiratory infections, and wheezing (Radojević and Bashkin, 2006; D'Amato *et al*., 2002 & Persinger *et al*., 2002) and can impair cardiovascular systems of the local inhabitants (Maitre *et al*., 2006). Nitrogen oxides reacts with other

atmospheric substance forming acid (Hashim *et al*., 2004; Kalabokas *et a*l., 2002 & WHO, 2000) which eventually fall as rain, fog, snow or dry particles (Gómez-Garcia *et al*., 2005). As such, they are capable of causing nutrient overload and deterioration of water quality (Bytnerowics *et al*., 2007), severe impacts on vegetation and materials (Alvim-Ferraz *et al*., 2006), weakening of the ozone layer (Gómez-Garcia *et al*. 2005), and global warming (Peace *et al*., 2004). As fog, nitrogen dioxide can reduce or impairs visibility.

2.8.3 Sulphur Dioxide (SO_2)

2.8.3.1 Sources

Sulphur dioxide is an undesirable and harmful pollutant resulting from, or as an aftermath of, human activities such as industrialisation, mining and other industrial processes involving the burning of fuel such as oil and sometimes coal (Soylu, 2007). They are emitted directly into the air from combustion of sulphur-containing fossil fuels such as coal, oil, and natural gas (Reddy and Venkataraman, 2002a, b). Isobe *et al*. (2005) established that the quantity of sulphur released by the emissions of coal combustion processes is higher than that by other fossil fuels (**Figure 2.4**). A mobile source of sulphur is also possible due to the presence of sulphur in motor fuel (Soylu, 2007) while volcanic eruption is a possible natural source of sulphur dioxide (Richards *et al*., 2006).

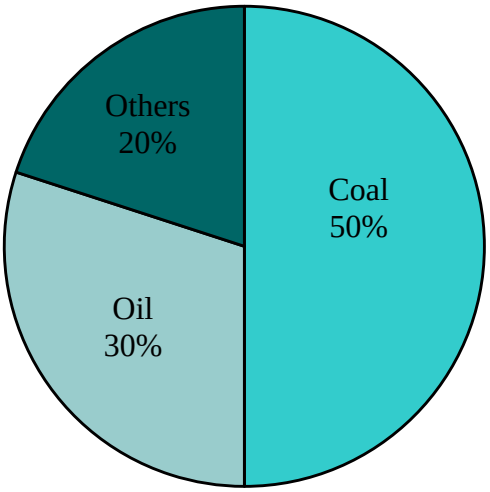

Figure 2.4: Sources of SO_2

Source: Air Pollution (www.air-quality.org.uk) - accessed 5th July 2011.

2.8.3.2 Epidemiological and ecological concerns of Sulphur Dioxide

Previous air pollution disasters, including the London smog of 1952, have been linked to the synergy of sulphur dioxide with smoke. As a precursor of sulphuric acid when released into the atmosphere, sulphur dioxide is known as a major contributor to acid rain which causes damaging effects including corrosion of stones, metals (Radojević and Bashkin, 2006) as well as contributing to environmental deterioration and observed ecosystem damage (Lee *et al*., 2008 & Kashulina *et al*., 2003). Acid rain has also been reported as a major contributor in deforestation by contamination of the northern hemisphere and is capable of causing biological death of lakes and rivers (Gómez-Garcia *et al*. 2005) and infrastructural damage such as leakages of corrugated roofing sheets (Pires *et al*., 2008). Sulphur dioxide can also react with other chemicals in the air to form sulphate particles which, when inhaled can result in corresponding

respiratory symptoms and diseases, difficulty in breathing, and premature death (US Environment Agency, 2004). Epidemiological studies (*e.g*. Pires *et al*., 2008 & Richards *et al*., 2006) have consistently shown that sulphur dioxide is a major air pollutant capable of causing irritation of the eyes and respiratory system, reduced pulmonary functions, exacerbate respiratory diseases including asthma, chronic bronchitis and emphysema, as well as causing breathing difficulties on direct exposure to its high concentrations. At high concentrations, sulphur dioxide can cause damage to plants including degradation of chlorophyll, reduced photosynthesis, raised respiration rates and changes in protein metabolism. Sulphur dioxide emissions can also contribute to acidification of soils and waters and subsequent loss of biodiversity, often at locations far removed from the original emissions (Defra, 2010).

2.8.4 Hydrocarbons

2.8.4.1 Sources

Hydrocarbons represent a mixture of chemical species generated from a wide source of combustion processes although road traffic and recognised as the major source in urban areas (Vardoulakis *et al*., 2008). Previous investigations revealed that hydrocarbons originate mainly from industrial activities such as residential heating, power generation, and incineration, in the wake of either unburned or incomplete combustion of fuel components and other organic substances (Dyke, *et al*., 2003) for which motor vehicle exhaust is of most significance (Lim *et al*., 2007). The estimated value for which hydrocarbon is accountable for in total vehicle emissions ranges from 75-96% in some cities (Dong *et al*., 2000). This is not surprising considering the upsurge in vehicular population and usage that parallels the increasing demand for fuel, thus, there is the potential of a concomitant release of major air pollutants. In

addition, road dust studies confirmed diesel vehicle exhaust, tyres and pavement as major contributors of PAH (Murakami *et al*., 2005; Pengchai *et al*., 2005) from the urban environment (Li *et al*., 2005) (**Figure 2.5**)

Other significant sources include stationary sources and solid waste disposal. Biological sources, coalfields, natural gas from petroleum fields, and natural fires, irrespective of their individual contributions, are some common natural sources of majority of hydrocarbons. Hydrocarbons could act as primary toxic pollutants, precursors in the formation of photochemical oxidant species (Caplain *et al*., 2006), or actively involved in photochemical reactions (Monod *et al*., 2001) and are ubiquitous in air especially in urban areas (Srivastava, 2004).

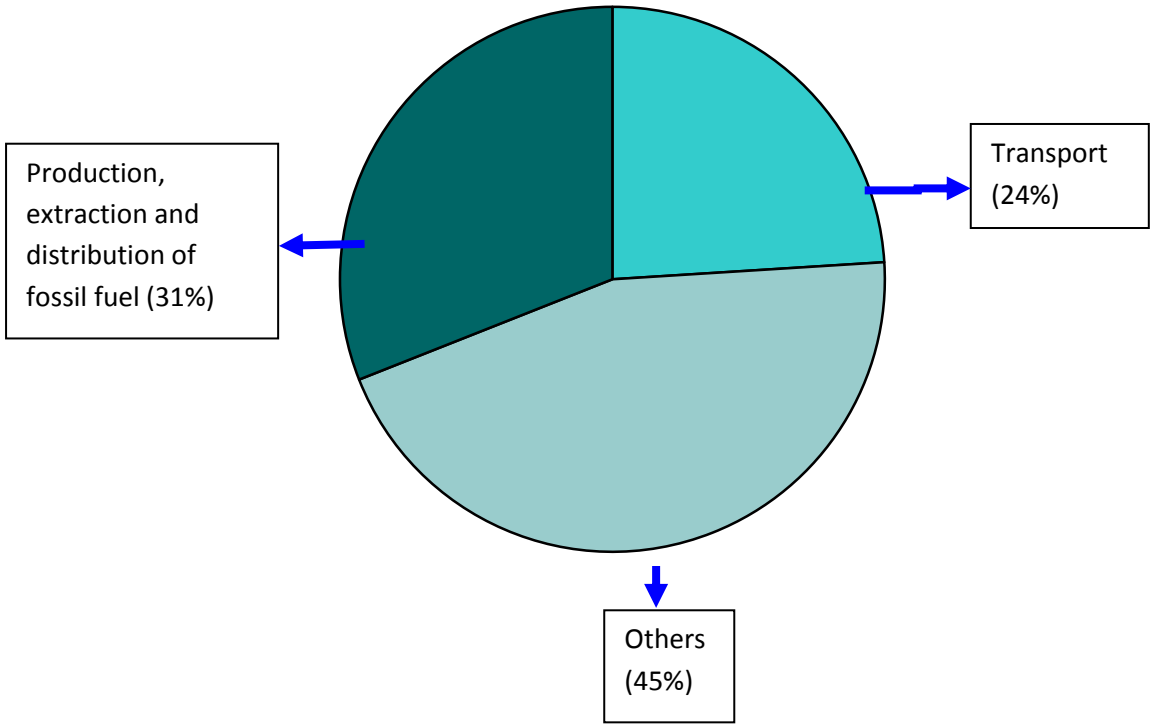

Figure 2.5: Sources of hydrocarbon
Source: Air Pollution (www.air-quality.org.uk) - accessed 5th July 2011.

2.8.4.2 Epidemiological and ecological importance of hydrocarbon

Hydrocarbons are hydrophobic in nature and less soluble, features that make them recalcitrant to biodegradation (Zhu *et al*., 2008). This means hydrocarbons accumulate and persist in the environment, and known as persistent organic pollutants (POPs), thus presenting a long-term threat to human health that justifies the epidemiological concerns it attracts. In determining the uptake of POP into leaf and their deposition on plant surfaces, the morphological characteristic of the leaf plays a key role. For instance, plants with hairy leaves are up to eight times more efficient at scavenging lead (Pb) in petrol exhaust than leaf surfaces without hairs (Howsam *et al*., 2000). The accumulation of POP in plants depends, largely, on plant surface characteristics, lipid contents and ambient temperatures and varies by several orders of magnitude that partly reflect different levels of atmospheric pollution (Franzaring & van der Eerden, 2000). Different plant species have been used to assess both environmental and epidemiological fate of exposure to persistent organic pollutants and are likely to cause significant adverse human health or environmental effects near to, and distant from, their sources. Some of them have been reportedly characterised by relatively high carcinogenic and mutagenic properties (Vardoulakis *et al*., 2008) while some are proven environmental estrogens and at high levels are capable of causing adverse effects on organisms (Franzaring & van der Eerden, 2000).

2.8.5 Heavy Metals

2.8.5.1 Sources

Heavy metals are natural components of the earth's crust that are non-degradable and moveable by air and water. Wide varieties of sources, including combustion,

wastewater discharges, and manufacturing facilities are the common pathways to the environment (Kampa & Castanas, 2008). Road traffic represents one of the main sources of dispersion of heavy metal pollution (Hjortenkrans *et al*., 2006). This implies that the presence of heavy metals near roads may signify emissions of exhaust gasses, brake wear, tyre wear and wear of mechanical parts due to friction. Metals such as zinc, copper, barium, and lead originate from brake lining wear (Laschober *et al*., 2004) but heavy metals of concern associated with brake wear emissions include Lead, Zinc, Cadmium, Copper, Nickel, Antimony (Sb), and Chromium (Li *et al.*, 2001 & Sörme *et al*., 2001). Resuspension of soil and road dust also represent a major potential source for metal emissions (Thorpe and Harrison, 2008; Laschober *et al*., 2004). The presence of Zn, in addition to traces of Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni and Pb represent tyre or mechanical abrasion of body car part emissions, while Cd, Cr, Cu, Ni, Pb and V are exhaust fume emissions originating from fossil fuel combustion (Hjortenkrans *et al*., 2006). Other metals of concern related to vehicle tyres, especially because tyres have been linked to traceable levels of several metals, include Cadmium, Cobalt, Chromium, Copper, Mercury, Manganese, Molybdenum (Mo), Ni and Pb (Davis *et al*., 2001; San Miguel *et al*., 2002). Combustion of leaded petrol and motor oils commonly represent important sources of some heavy metals (Laschober *et al*., 2004). However, with the ban of leaded petrol in Europe, lead emissions from traffic has been considerably reduced, yet fossil fuel combustion remains the source of some emissions of Cd, Cr, Cu, Ni, Pb and V (Ozaki *et al*., 2004 & Cadle *et al*., 1999). Prior to the phase-out of leaded petrol, it has remained the major source of heavy metals with lead as the heavy metal mostly associated to traffic emissions (Rode *et al*., 2010) but currently, Cu, Zn, and Pb represent the most

important traffic-related heavy metals while the source of other heavy metals may vary (Van Bohem and Van de Laak, 2003).

Lead (Pb) is a heavy metal whose emission source is fuel combustion in road transport in Europe (Pacyna *et al*., 2007). Naveed *et al*. (2010) studied lead pollution of roadside using plant leaves as bioindicator, found higher deposition of heavy metals, e.g. lead, in plants near roadways, and therefore concluded that higher vehicular densities and the distance from roadways influenced this. Although there are other sources of Pb including smelting, fabrication processes or paint manufacture, disposal of unwanted lead-containing materials, and combustion of coal, Lam *et al*. (1999) revealed that lead discharged from automobile exhaust constitutes the major source of atmospheric lead.

Copper is another metal produced by transport and enters the air, mainly through release during the combustion of fossil fuels, and finally deposited on different surfaces including leaf, grass, and soil. The main sources are coal combustion, public power generation and road transport. Interestingly, the decline in oil and heavy fuel oil combustion has contributed to corresponding decline in Cu emissions (Dore *et al*., 2007).

2.8.5.2 Health concerns of Heavy Metals

Among the heavy metals, lead has become so important due to their toxicity and constant increase in the environment (Naveed *et al*., 2010). The common pathway of lead into human bodies include consumption of unwashed food supplies, especially those within the roadways, and inhaling contaminated air, especially pedestrians walking along heavily trafficked roadways. Lead can bio-accumulate in human body

and can become toxic at low dose concentrations (Järup, 2003). Lead has been associated to certain diseases that have lethal effects on man and animals (Silva *et al*., 2005; Michalke, 2003). On contact with the eyes and nose, Pb dust or fumes can cause irritation, and on inhalation, can cause irritation to throat. While the consequences of acute exposure to Pb include loss of appetite, weight loss, stomach upsets, nausea and muscle cramps, high levels of acute exposure may lead to brain and kidney damage and the resultant effect of chronic exposure can lead to effects on the blood, kidneys, central nervous system and vitamin D metabolism (Dore *et al*., 2007).

Exposure to Cu fumes can result in acute effects such as irritation of the eyes, nose and throat, coughing, wheezing and nosebleeds. Such exposure can also result in a flu-like illness with symptoms of a metallic taste, fever, chill, aches and chest tightness. Effect of chronic exposure to Cu may include decreased fertility in men and women as well as severe irritation and ulcers in the nose (Dore *et al*., 2007).

2.9 Conclusion

This chapter looked at air pollutants, their sources and contributions to air quality. Vehicular traffic remains the major source of air pollutants and both distance and height had significant influence on the concentration levels of pollutants. Different factors contributed to the temporal and spatial distribution of air pollutants including high traffic volume, meteorological parameters, landscape, and car and driving conditions. The epidemiological and ecological impacts of air pollutants elicit several adverse effects on human health, plant growth, infrastructural damages, acid rain, and global warming. These concerns necessitated the provision of set limits for the pollutants.

Chapter Three

Experimental Methodology

3.0 Introduction

The previous chapter reviewed different approaches for measuring different air pollutants. It is a common practice in air monitoring studies to carry out field sampling and subsequently prepare them for laboratory analysis. While some devices generate on-the-field data, others may need further laboratory preparations. This chapter will consider, in details, the different sampling techniques and their applications in generating useful data for the study analysis.

3.1 Study area and site description

The A49 trunk road is located in Shropshire in the area of Welsh Borders, England and runs north south through Shropshire. It serves as a connection between Cheshire and Merseyside, Hereford and South Wales, Shrewsbury, Ludlow and Whitchurch - all significant areas of population. The study area is a wide range of different types of place, including remote upland farmsteads, fishing communities, former mining areas, small market towns and sub-urban villages with some rural populations of between from 1,500 and 5, 600. The demographic description of the study area fit in the Rural/Urban definition of rural areas defined as places with communities of fewer than 10,000 people. They make up 86% of the country and are home to around 20% of England's population. Movement in the study area is predominantly by motor vehicles and the frequency of travel has significantly increased over the years as exemplified by road traffic growth of 3% per year (DETR, 2001).

Figure 3.1 illustrates the four pair of sampling sites. They were selected, one each from All Stretton (AS), Strefford (ST), Church Stretton (CS) and Craven Arms (CA) and the sample locations are shown on the map as CS1, CS2, CS3 (hereafter represented as CSW 100, CSW 50, CSW 5), CS4, CS5, CS6 (hereafter represented by

CSE 5, CSE 50, CSE 100), AS1, AS2, AS3 (hereafter as ASW 100, ASW 50, ASW 5), AS4, AS5, AS6 (henceforth as ASE 5, ASE 50, ASE 100), SR1, SR2, SR3 (from now on as SRW 5, SRW 50, SRW 100), SR4, SR5, SR6 (hereafter SRE 5, SRE 50, SRE 100), CA1, CA2, CA3 (represented afterward CAW 5, CAW 50, CAW 100) and CA4, CA5, CA6 (subsequently represented as CAE 5, CAE 50, CAE 100) respectively . The sites are adjoining minor roads, farm roads, or walkways located at both sides of, and running perpendicular to, the A49 trunk road. The All Stretton and Strefford sections of the A49 trunk road are single carriageways while Church Stretton and Craven Arms sections are dual and characterized by different traffic volumes. All four sites comprise of both east and west sides of the A49 road.

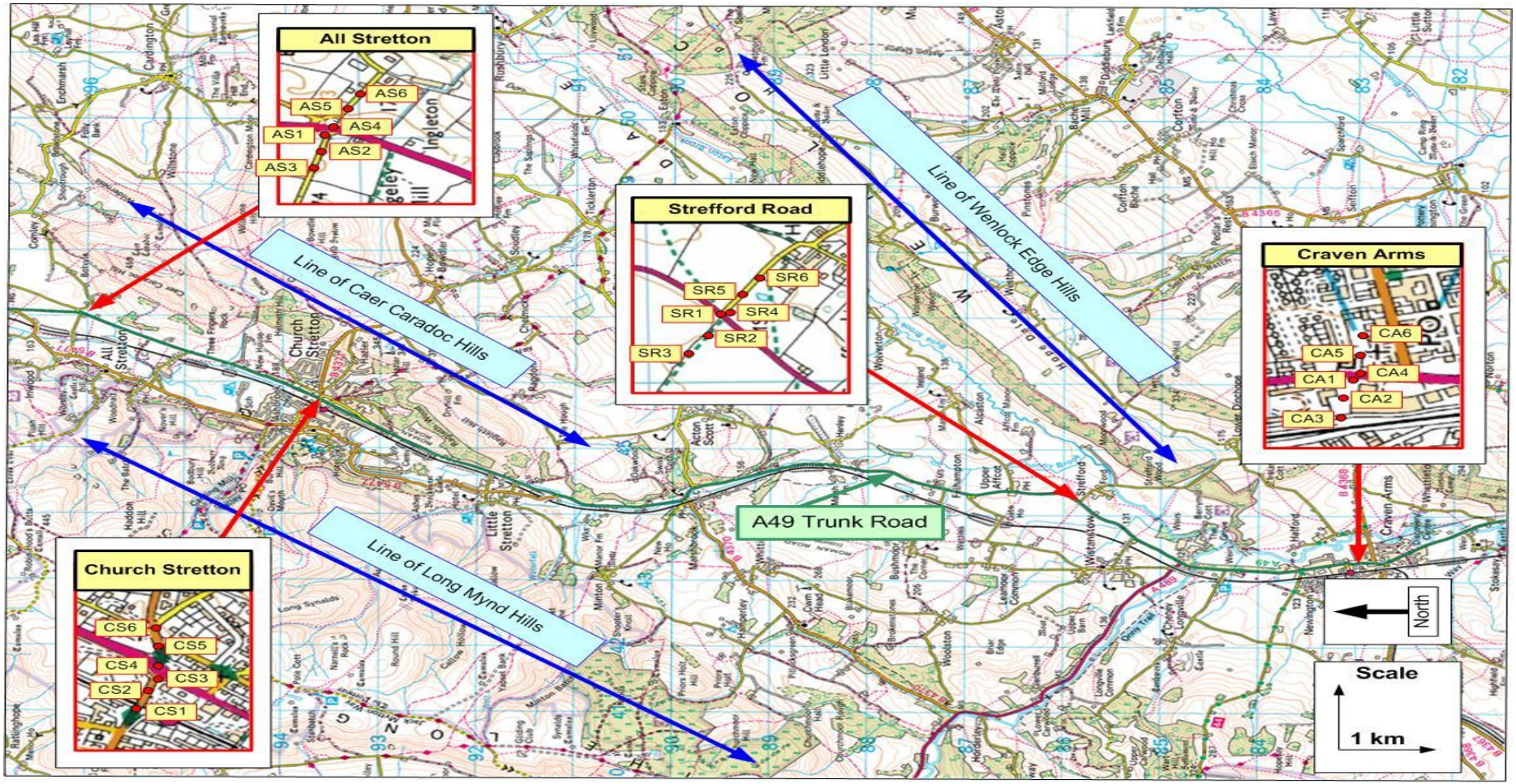

Figure 3.1: Location of Sample Sites close to A49 Trunk Road
Specific sample locations (CS1 - CS6, AS1 - AS6, SR1 - SR6 and CA1 - CA6) are indicated by the red circles on each of the four map inserts (Map - 1:25 000 OS Explorer Map, Sheet 217, the Long Mynd and Wenlock Edge)

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The common topographic feature of the study area is the South Shropshire Hills (**Plate 3.1**) which runs parallel to the A49 trunk road, effectively channelling the prevailing wind to the north easterly along the A49 trunk road. This is capable of forming a partially enclosed volume that can greatly affect atmospheric mixing and transport, a process often described as "canyoning effect".

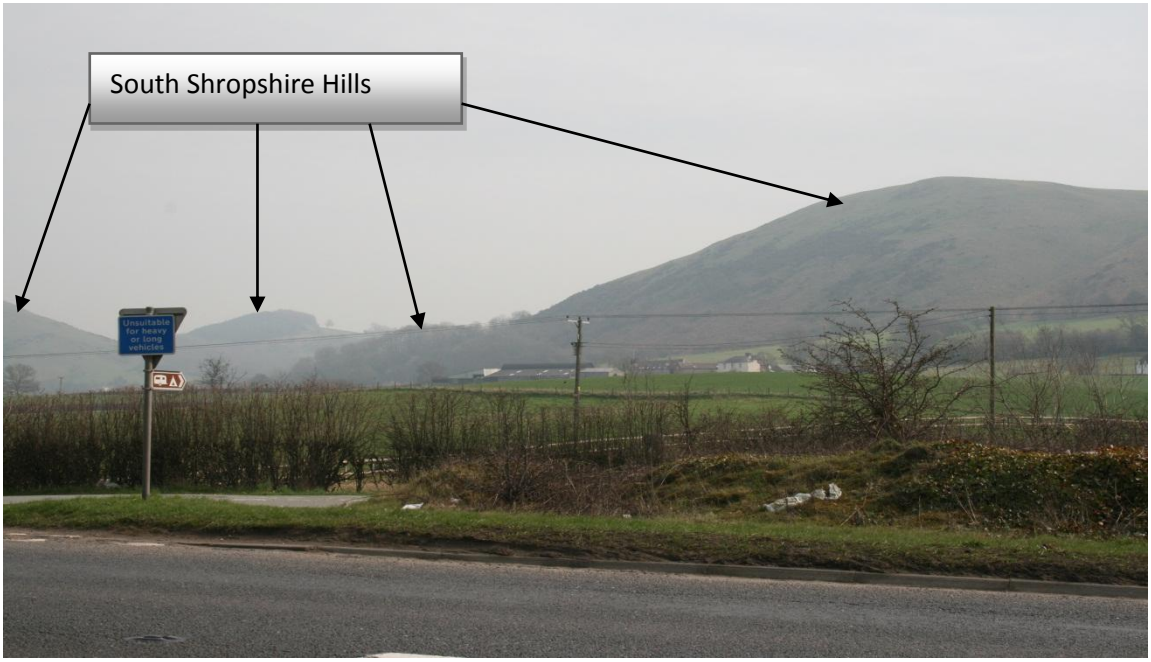


Plate 3.1: Topography of the study area

3.1.1 Strefford site

This road provides access to livestock farmhouses and a rural community with few domestic houses (**Plate 3.2**). The sampling sites were designated Strefford East (STE) and Strefford West STW). Lying directly opposite the STE Road is a Farm Road, which serves as the sample site location for STW (**Plate 3.3**). The road provides access to livestock farmhouses, grazes fields, and flanked by maintained shrubs. Both STE and

STW roads are characterised by low traffic and flanked towards the north by South Shropshire Hills that runs parallel to, and about 1000 m from, the A49 trunk road. The surrounding of both sites is dominated by agricultural areas and grazing fields that are often grazed by livestock, implying regular up and down movements of livestock at this site.

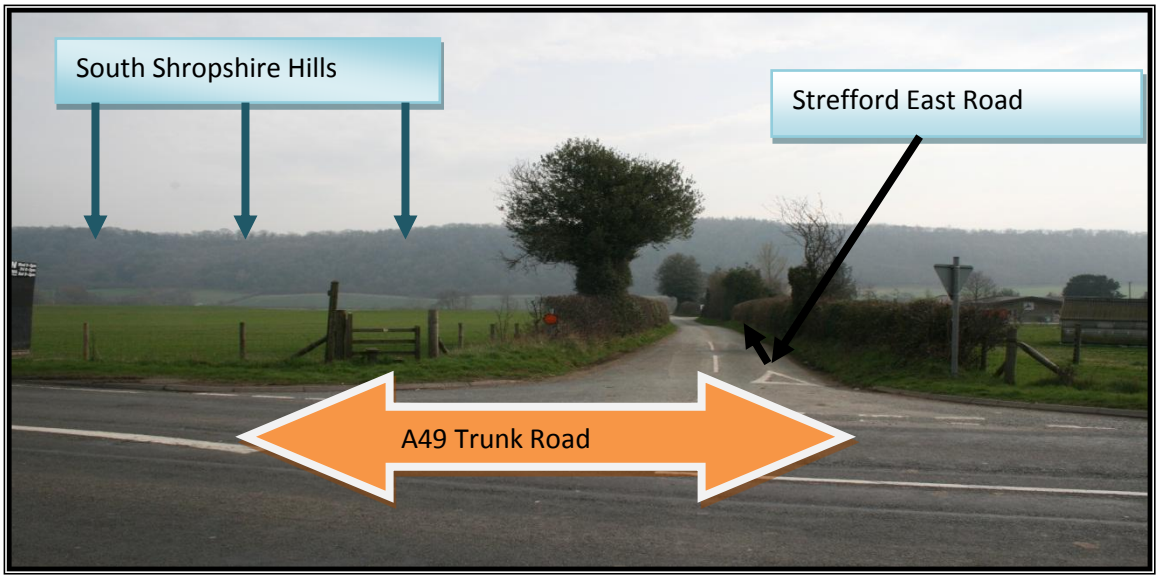


Plate 3.2: Strefford East sampling site

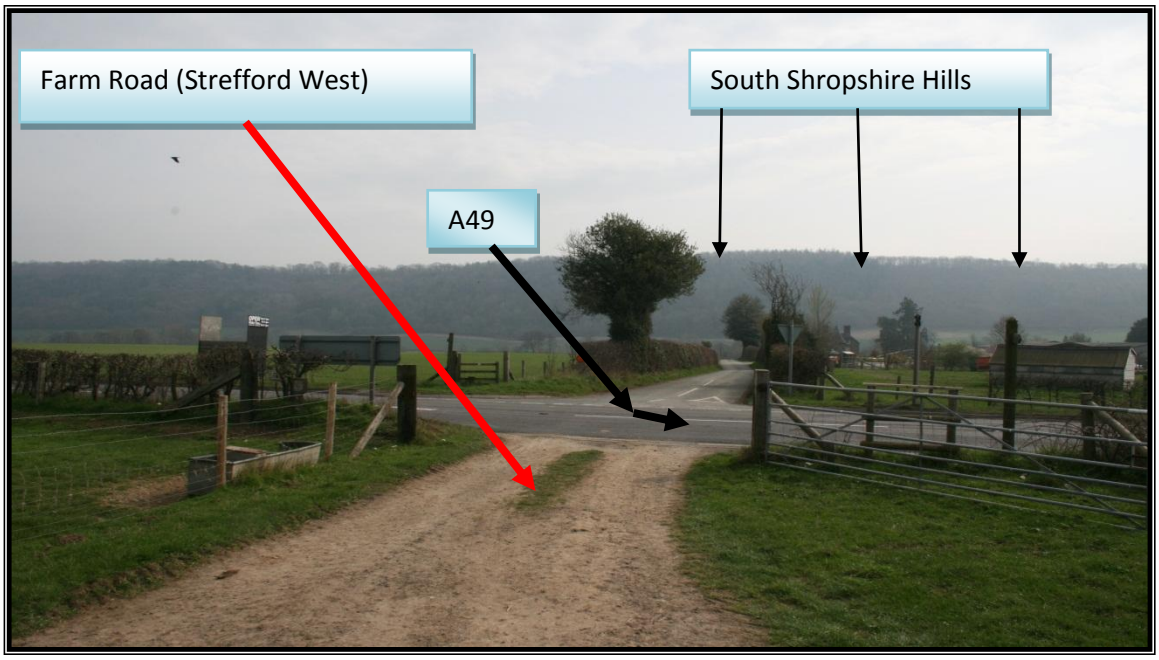


Plate 3.3: Strefford West sampling site

3.1.2 All Stretton Site

This pair of minor roads lies east and west of the A49 trunk road and designated All Stretton West and All Stretton East (**Plates 3.4 and 3.5**). They are about a mile apart from the All Stretton site and as such are characterised by similar traffic volume, given that they provide access to few residential and farm houses. The sites also share the same landscape and topography as All Stretton site, being surrounded by agricultural areas, grazing fields, and bordered towards the north by the South Shropshire Hills that run perpendicular to the sampling road sites and parallel to the A49 trunk road. This site is characterised by livestock activities such as grazing and milking, suggesting that livestock regularly go up and down this site.

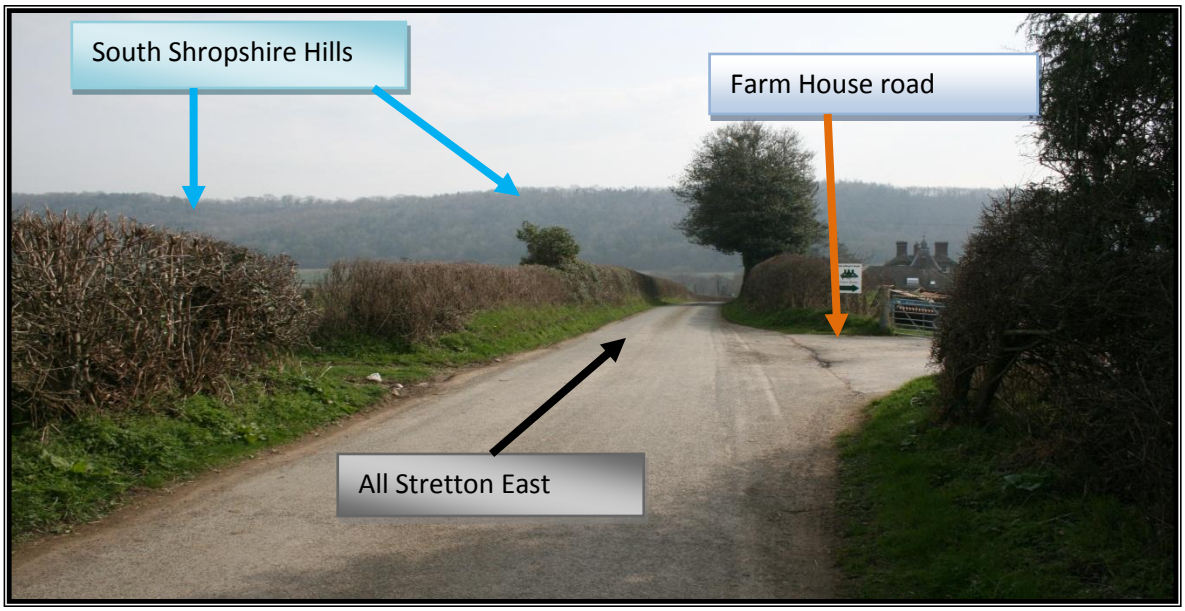


Plate 3.4: All Stretton West sampling site

Plate 3.5: All Stretton East sampling site

3.1.3: Church Stretton site

Church Stretton is a mix residential and commercial area and is usually characterised by busy traffic at peak periods especially because this section of the A49 connects

population destinations. This site features the South Shropshire Hills, a train line, few moderately trafficked B roads and park. Two opposite trunk B roads (signifying Church Stretton East and Church Stretton sampling sites) abutting the A49 trunk road was selected for sampling. Both roads extend from a busy junction with sets of traffic light to the A49 road (**Plate 3.6**). Thus, majority of the traffic flow characteristic of this site was slow moving or idling. At Church Stretton East there are two minor roads (one on the right lane near the 50 m and the other on the left lane near the 100 m distances) leading to few residential buildings. With a wait in turning into the minor road near the 50 m, there was traffic flow delay at this point. In contrast, traffic flow into the minor road near the 100 m sample point is usually not characterised with any traffic delay. **Plate 3.7** shows the train line near this sampling site.

Plate 3.6: Church Stretton East and West sampling sites

Plate 3.7: Train line near Church Stretton

3.1.4: Craven Arms site

Craven Arms is located about 7.5 miles away from the Church Stretton site location and serves as conduits to larger communities lying adjacent to the A49 road. This site is a built-up area comprising of both residential and retail outlets, and a mini roundabout junction. To the east of the site (Craven Arms Road East – **Plate 3.8**) is a petrol station, a train line (about 300 m behind the petrol station), a big retail shop and a car park which adjoins the petrol station, thus providing car-parking services to both. To the west of the sampling site (Craven Arms Road West – **Plate 3.9**) is a footpath lying directly opposite a petrol station and extends to a car park that services both the residential buildings and retail shops. Common driving scenarios at this site location include regular breaking, accelerating and cruising

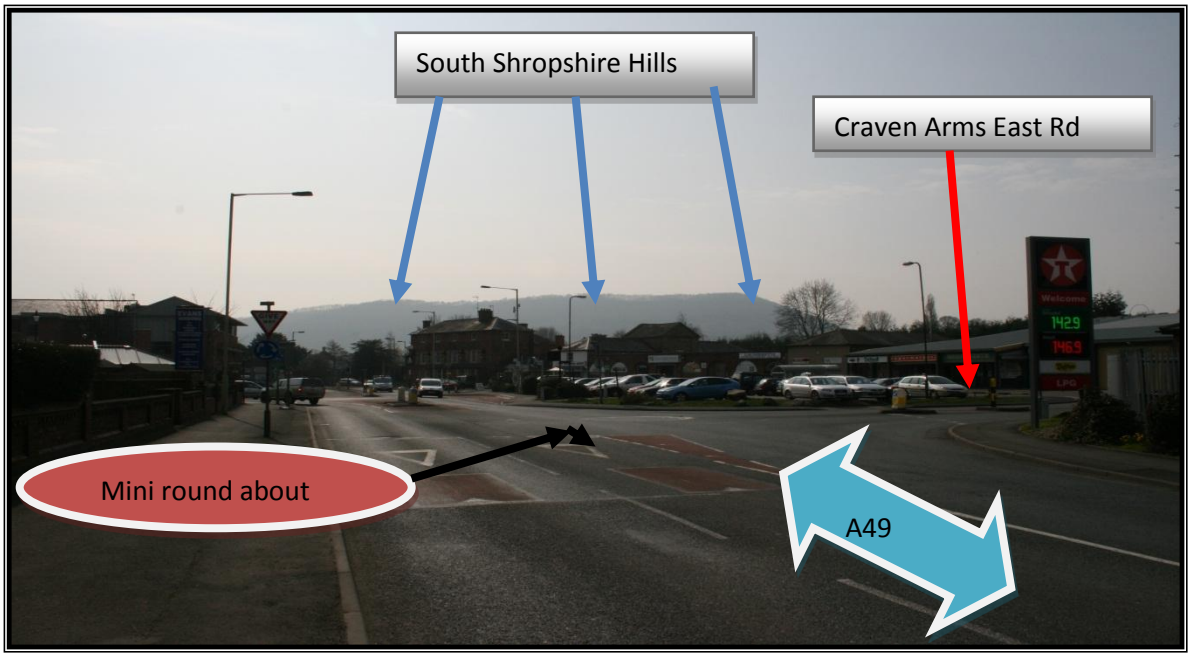


Plate 3.8: Craven Arms East sampling site

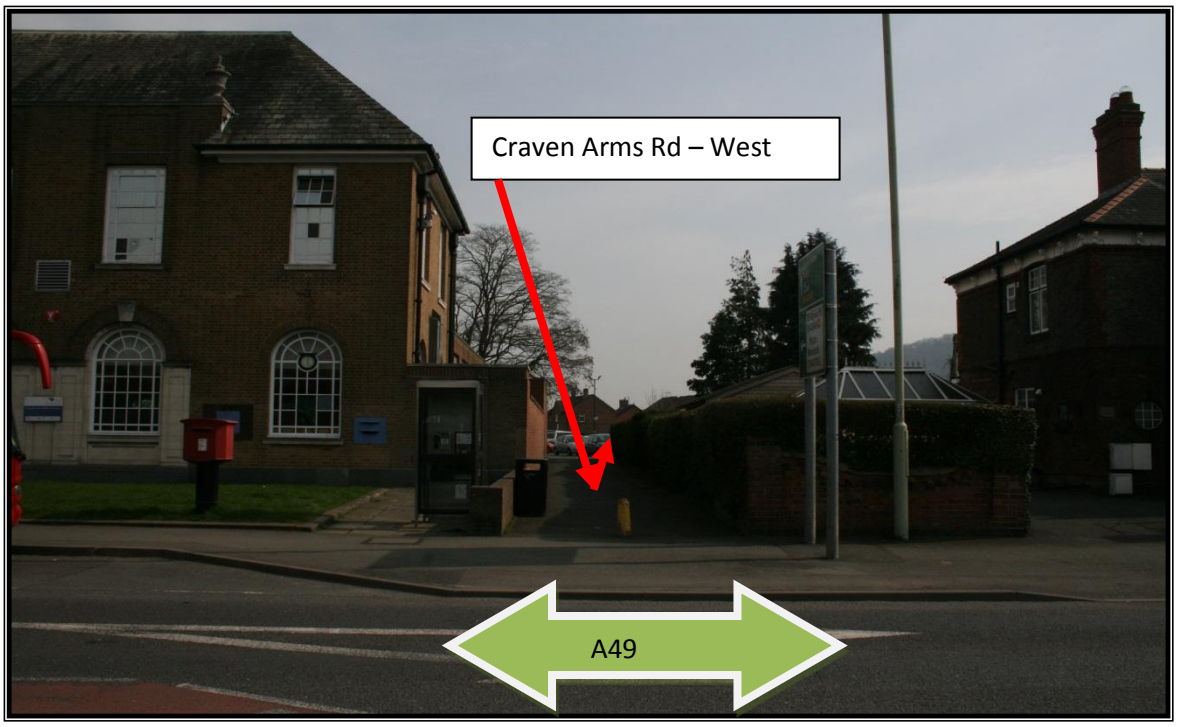


Plate 3.9: Craven Arms West sampling site

3.2 Sample locations

Distance from emission source is of paramount importance to air quality monitoring due to increasing interest in exposure studies. Accurate distance was determined by the application of Laser Rangefinder (Bushnell Range finder – Model V2), a hand-held device that makes measuring distance quick and effortlessly easy. The GPS of the sample points are as shown in **Table 3.1** and on the map (**Figure 3.1)**.

Table 3.1: GPS of sample locations

Sample distance from A49 road	All Stretton		Strefford		Church Stretton		Craven Arms	
	East	West	East	West	East	West	East	West
5m	E347057 N296100	E347031 N296070	E344211 N285844	E344195 N285851	E345771 N293631	E345745 N293634	E343309 N282869	E343297 N282882
50m	E347079 N296065	E346995 N296076	E344239 N285617	E344157 N285867	E345805 N293630	E345739 N293679	E343346 N282869	E343256 N282890
100m	E347098 N296033	E346957 N296087	E344122 N285893	E344272 N285794	E345850 N293629	E345729 N293713	E343383 N282865	E343217 N282892

3.3 Sampling methodology

Samplings were on both pairs of site locations at different distances of 5, 50, and 100 m from the A49 trunk road. During sampling, a buffer distance of 5 m from the trunk road was allowed to cushion the effect of traffic-induced turbulence. Thus, measurements started from 5 m away from the edge of the road, representing the roadside sampling point.

3.3.1 Traffic Survey

Traffic frequency was determined manually by counting the number of vehicles passing on both sides of the trunk road between 08:00 and 12:00 hours on a typical working day throughout the sampling period. Vehicle classification was determined by aggregating individual vehicle types and three major vehicle categories (heavy-duty vehicles, light goods vehicles, and passenger cars) were recorded.

3.3.2 Meteorological Conditions

Measurements of meteorological conditions at the selected site locations was continuous (once every month) for 22 months and were conducted in the morning rush hours in typical working days when traffic emissions are evident. Wind speed was measured using Pocket Wind Meter (Kestrel 1000), a small electronic rotating vane type of anemometer that uses high precision jewel bearings and a light weight impeller to provide accurate wind and air flow measurements even at low speeds. CEM DT-8820 measured relative humidity and temperature.

3.3.3 Gas detector tubes

The gaseous pollutants were monitored using Dräger tubes. The short-term Dräger tubes were pre-calibrated for two years and designed for on-the-spot gas detection at a particular location over a relatively short time. They are suitable for measuring the instantaneous levels of air contaminants at any given time and thus provide quantitative data of gaseous air contaminants. If the targeted chemical is present, the reagent in the tube changes colour and the length of the colour change typically indicates the measured

concentration. Advantages of Dräger Short-term tubes include easy reading, fast, accurate, specific measurements, and they do not require any sort of maintenance. They are available in different types for different gases and determination of gaseous concentrations is usually by visual colorimetric comparison. Setting up the device requires a hand-held bellows-type pump (Accuro) designed with a restraining chain into which a new tube is inserted for each analyte (**Plate 3.10**). The tubes draw air sample through the calibrated 100 millilitre Dräger tubes that normally come sealed from the manufacturer and opened at both ends using a Dräger tube cutter (**Plate 3.10**) just before sampling. Air sampling followed the instructed procedures, inserting new tube into the hand-held pump and pumping as instructed on the tube.

Plate 3.10: Unused Dräger tube and a tube cutter (left) and Dräger tube pump (Accuro) (right)

Source: Dräger (www.draeger.com/UK/en/products/gas_detection/tubes_cms/pumps/cin_accuro.jsp): (accessed 20th June 2011)

3.3.3.1 NO_2 and SO_2 short-term sampling

Monthly concentrations of NO_2, SO_2, and hydrocarbons were monitored in all four sites in the order of 5, 50, and 100 m distances from, and along the transect perpendicular to, A49 trunk road. The roadside sampling distance from the edge of the road was 5m, representing the buffer from the trunk road, to reduce traffic-induced turbulent effects (Ainslie *et al*., 2008) and about two meters above ground level to represent the breathing zone (as Lau *et al.*, 2008 & Defra, 2007). Measurements took place between 08:00 and 12:00 hours on a typical working day, once every month for 22 months.

3.3.4. SO_2 and NO_2 sampling using diffusion tubes

Diffusion tubes (passive sampling tubes) measure SO_2 and NO_2 pollutants over a given period. This technique allows the quantification of cumulative air pollutant and is attractive for air quality investigations at various scales (Farrar *et al*., 2005, Harner *et al*., 2003 & Wania *et al*., 2003). Detail of this technique including the advantages of its applications is as discussed in section 2.1.2.

Nitrogen Dioxide (NO_2) and Sulphur Dioxide (SO_2) were monitored at four selected sites using passive diffusion tubes on a seasonal basis. Only the mid-seasonal concentrations were analysed to ensure that measurements accommodate seasonal representative samples intended. Measurements were conducted three-weekly in the order of roadside 5, 50 and 100 m. At each sample site and location, two passive tubes (one for the monitoring of SO_2 and one for NO_2) were set up vertically at a height of about 2 m above ground level to avoid interference by local fauna (Laffray *et al*., 2010) as well as

representing the breathing zone (Truc and Kim Oahn, 2007). Tubes were mounted with the open side facing down to avoid any interference such as rain. The three-weekly exposure period was useful to develop the time-weighted average (TWA) which will provide the knowledge of average concentration of the analyte over that period of time (Seethapathy *et al*., 2008). The results, indicated by color change, were expressed in parts per million (ppm) and the average concentration value was determined by dividing the total concentration by total time (in hours) of the exposure period as shown in equation 3.1.

$$MC = \frac{Tc}{Tt} \qquad \text{..... (Equation 3.1)}$$

where M_C = mean concentration; T_C = total concentration; T_t = overall time regime (21 days x 24 hours = 504 hrs.)

3.4 Vegetation Sampling

The use of vegetation as biomonitors for air monitoring studies has been reported (Fuga *et al*., 2008) and enjoys the advantage of low-cost and easy sampling (Bermudez *et al*., 2009) as discussed in section 2.1.1.

3.4.1 Sample collection for analysis

The sample collection and laboratory procedures (preparation), according to Heumann (2002), are the most important aspect in analytical techniques. The sampling design was to collect hazel leaf (*Corylus avellana*) and ryegrass (*Lolium perenne* Linnaeus) samples in all four sampling sites once per season (winter-spring-summer-autumn) between June

18, 2008 and April 6, 2010. However, hazel leaf was not sampled at Craven Arms sampling site because it was not found at the vicinity if the sampling locations. Because hazel plant is deciduous, leaf sampling was restricted to the growing seasons of spring (April) and summer (July) to ensure that collected samples were fresh, damage- and disease-free. Ryegrass samples were collected at all four site locations during both sampling periods. To reduce the chance of variability of results, sampling was limited to only samples that were not past full maturity age, or visibly damaged or dead. For true representativeness of the samples, a 2 x 2 quadrant random sampling procedure was adopted. One hundred grams each of fresh hazel leaf and ryegrass samples were collected from each sampled site location with a pair of scissors and properly sorted to exclude unwanted materials. The samples, loosely packed in polythene bags, labelled accordingly in the order of roadside (5m), 50, and 100m, and immediately transported to the laboratory for analysis. **Figure 3.2** presents a flow chart of the analytical procedures of vegetation samples and their particulate deposits.

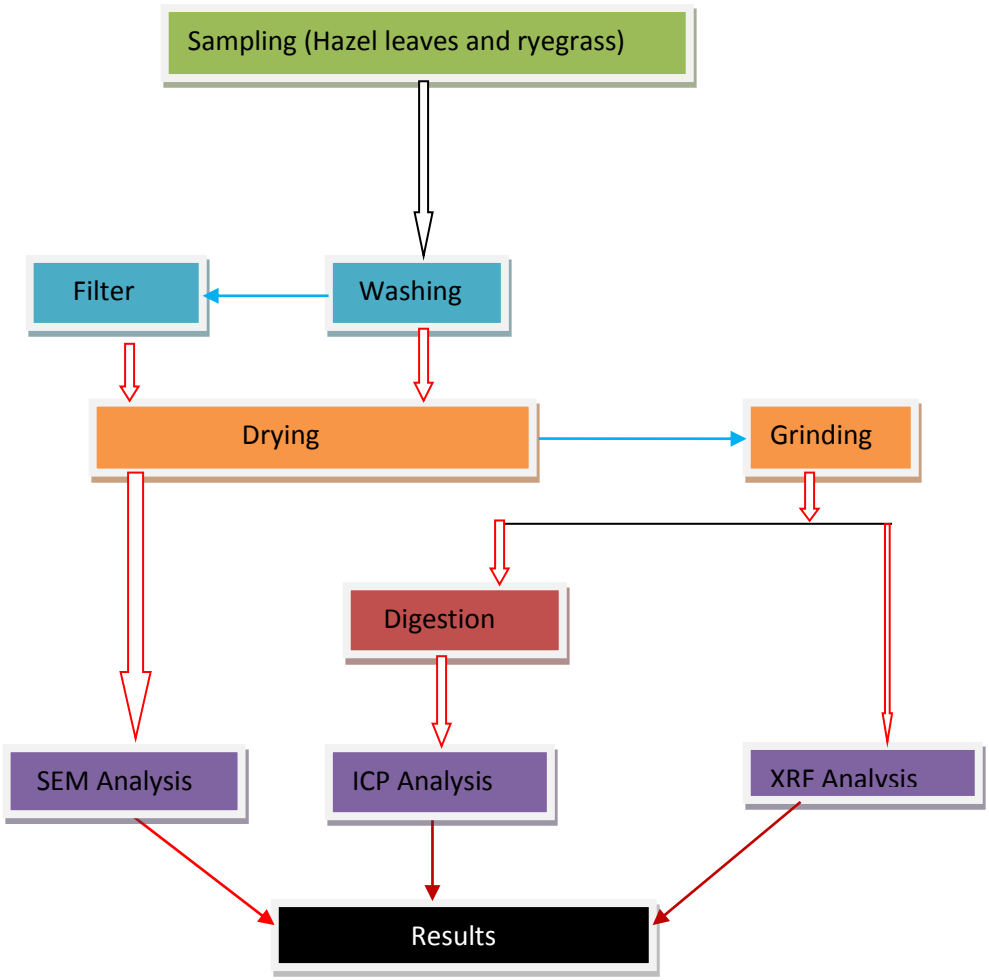


Figure 3.2: Flow Chart of vegetation sample collection and analysis

3.4.2 Procedure for X-ray Fluorescence Spectrophotometry (XRF) analysis

XRF is an analytical method commonly used for multi-elemental particle detection and analysis (Calzolai *et al*., 2008 & Colls, 2002) and can detect elements even at low concentrations (Carvalho *et al*., 2001). Major strengths of this technique are in providing one of the simplest, economical and accurate analytical methods for the determination of the chemical composition of many types of materials, providing detection limits at the sub-parts per million levels, ease of use, and for non-destructive and non-conductive

material applications. The application of this technique is significant because the deposition of particulate materials on leaf surfaces can initiate uptake processes of some contaminants. The absorbed elements are then determined using XRF. According to Bakker *et al*. (2000), the uptake processes begin with the transportation of atmospheric contaminants to the laminar air boundary layer around the leaf and afterwards, across the boundary layer where the interaction of the deposited contaminants with the leaf surface is initiated.

Washing: The concept of washing the plant samples was to remove the surface dust or soil mineral particles in order to reduce local contamination (Rey-Asensio & Carballeira, 2007) and to avoid leaching of some of the chemical components that may interfere with some analysis and contribute to variability. Fresh plant materials transported to the laboratory, placed into different empty acid-washed 600 ml crucibles filled with water and subsequently transferred into a sonic bath (DP201-00) where dust and particulate loadings on the vegetation samples were dislodged.

Drying: Homogenisation of sampled plant materials is easier when the samples are dried. Drying also minimises biochemical changes that may interfere with some analysis. The vegetation samples were oven-dried at 40^{o}C for 24 hours immediately after washing.

Grinding: To obtain a representative sample suitable for further treatment and analysis, the oven-dried washed plant materials were subsequently ground to powder using an electric grinder (A10 - JANKE & KUNKEL: IKA WERK).

Analysis: One-gram portion of loose ground plant materials from each sample was weighed, labelled and sent for XRF (SPECTRO XEPOS) to analyse for Al, Ca, Cr, Cu, Fe, Mg, Mn, Si, Zn and Pb.

3.4.3 Procedure for Inductively Coupled Plasma (ICP) analysis

Used for the detection of trace metals in environmental samples, this analytical technique has the advantage of identifying and quantifying all elements (apart from Argon). Another advantage is in accomplishing a multi-elemental analysis very quickly (in some cases, 30 seconds).

The procedures for ICP analysis are similar to XRF up to the grinding stage as discussed in section 3.4.5.2 and shown in figure 3.2 in addition to:

Digestion: Ground vegetation samples (0.5g each) were digested in a mixture of 6 ml nitric acid and 1 ml hydrogen peroxide using microwave digester (Ethos 900) operated at 1200W with pressure incrementing from 80 to 150 psi for 30 minutes.

Analysis: The digest was made up to 50 ml with de-ionised water and analysed for As, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Sb, Sr, and Ti using ICP (SPECTRO CIROS ^{CCD}).

3.4.4 Procedure for Scanning Electron Microscope (SEM-EDXS) analysis

The combination of Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy is a non-destructive solid analytical method often used to characterize the mineralogical phase of individual particles. The application of Scanning Electron

Microscopy for the identification and quantification of airborne particulates distributed on biological materials from multiple pollution sources has been reported (Suzuki, 2006), and SEM (ZEISS EVO 50) apparatus equipped with EDXS system the preferred choice of measuring the pollutant element profile on the surface of the leaf and grass samples (Tomaševic´ *et al*., 2005). Catinon *et al*. (2009) determined the particle content of a plant material by analysing the sieved deposits using SEM-EDXS. The procedural processes are as outlined in figure 3.2 and discussed in the following section:

***Filtration*:** Particle loads eluted from the washing process described in section 3.4.5.2 were filtered using cellulose filter paper (Whatman 42) designed for general filtration. The filter paper provides suitable particle retention levels of up to 2.5µm. The set up involved retort stand, clamp, flask, and pressure pipes similar to the method suggested by Kaur *et al*. (2007). As filtration progressed, the pressure valve was repeatedly adjusted to regulate the suction effect of the filtration process and deposited particles collected on the filter paper as retentates.

***Drying*:** The filter papers (stuck with the retentates) were oven-dried for ten minutes at 40 ^{0}C and afterwards sealed in clean Petri dishes and sent for analysis by SEM-EDXS.

***Analysis*:** The collected retentates from the resultant dry filter papers were mounted onto aluminium stubs over double-sided stick tape on carbon discs of SEM (ZEISS EVO 50) and sputter coated in gold, essentially to minimize charging of electrons on the samples. For the imaging and elemental analysis of particles deposited, SEM was equipped with energy dispersive x-ray spectroscopy (EDXS) which produced beam of electrons that hit the samples and are converted into images that are subsequently relayed onto the screen.

Particles were observed by backscattered electron images as particle morphologies. The elemental components determined using this analytical technique include Al, Si, C, S, Cl, P, K, Ca, Na, Mg, Fe, Cu, Zn, Mn, and Ti.

3.5 Statistical Analyses

Where applicable, results were analysed using Microsoft Excel 2010 statistical software package. Statistical tests such as analysis of variance (ANOVA) and paired t-test were used for data analysis to compare data and check for significant differences in concentration profiles between pollutants and distances from the road. Analysis of variance (Anova) were carried out for significant differences (statistically significant at $P \leq 0.05$, * $P < 0.01$, ** $P < 0.001$, *** $P < 0.0001$ and statistically insignificant at $P > 0.05$). Statistically significant difference between pollutants or elemental concentrations will connote that the trend observed in the spatial distribution of that variable is relatively not uniform as opposed to when statistical difference is not significant, depicting that the measured variables are comparatively uniform. Where appropriate, data sets were analysed with descriptive statistics, particularly average mean and standard deviation to get a complete picture of emission distribution. Data sets with small standard deviation from the mean were interpreted as tightly grouped and precise data in contrast to those with large standard deviations inferred as data spread out over a wide range of values.

To understand the relationship between dependent variables (traffic frequency on one hand and meteorological parameters, e.g. wind speed, temperature, and relative humidity, on the other) and pollutants (independent variables) at each pair of sampling sites, regression analyses were carried out with the dependent variables plotted on the y-axis

against the independent variables on the x-axis. The closer R and r^2 are to one, the higher the trend of predictability of the influence of the dependent variable on the independent and/or vice versa. For the purposes of assessing compliance of various pollutants with the NAQS, results were converted from parts per million (ppm) units to microgram per cubic meter ($\mu g/m^3$) using equation 4.3. In doing this, concentration data of pollutants of interest beyond detection limit were equated to zero.

$$\mu g / m^3 = \frac{ppm \times MW}{0.0224} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.3)$$

Source: (Gary, 1987)

Note: $\mu g/m^3$ = micrograms per cubic meter (micrograms of gaseous pollutants per cubic meter of ambient air); MW = molecular weight of the gaseous pollutants; ppm = parts per million (volume of gaseous pollutant per million volumes of ambient air); and 0.0224 represents the volume (litres) of a mole of a gas.

3.6 Conclusion

This chapter described the study area and the sample site locations. Data for analyses were generated from field samplings using different hand-held devices and from the laboratory, using different analytical techniques. Laboratory preparations of samples for analyses followed different procedures suitable for the appropriate analytical methods such as X-ray fluorescence (XRF), Scanning Electron Microscope (SEM-EDXS), and Inductively Coupled Plasma (ICP) were also reported in this chapter.

Chapter Four

Results

4.0 Introduction

In the previous chapter, data from several sampling devices and various experimental methodologies, in addition to details of statistical analysis employed for data interpretations were considered. This chapter presents the field and experimental data from the 22-month sampling period (between June 2008 and April 2010). The results are presented in subsections by samples and where applicable, by seasons. Analysis for statistical significance between samples, site locations and the influence of meteorology and traffic volume on the concentrations of pollutants are also presented in this chapter.

4.1 Meteorological Data

The meteorological field data including temperature, relative humidity, and wind speed are as shown in **Appendix 1**. The Wind direction in the study area was predominantly north-easterly with maximum wind speed of 3.1 m/s recorded in June 18, 2009 (summer) and the minimum of 0.4 m/s observed in January 22, 2009 (winter) in All Stretton and Craven Arms site locations respectively. The maximum temperature was 18^{o}C in Church Stretton and Craven Arms in August 20, 2009 while minimum temperature of 7^{o}C was observed in January 15, 2010 (mid-winter) at All Stretton and Strefford site locations. Similarly, the maximum relative humidity of 69% was observed in mid-winter (January 15, 2010) in All Stretton and minimum (41%) in July 8, 2008 (summer) at Craven Arms site location. Part of the meteorological data from Church Stretton and Craven Arms site locations were lost in the laboratory so are not included in the data analysis.

4.2 Traffic Data

Although traffic surveys have the limitation of only providing data of specific locations at certain times rather than covering the entire study time, the application of data from traffic surveys is desirable if information of actual traffic patterns on real-carriages is required. The objective of the traffic data collection was to evaluate the relationship between variation in traffic frequency (volume) and concentrations of pollutants. The total counted vehicle volume was 6, 892 in All Stretton, 6, 860 in Strefford, 11, 108 in Church Stretton, and 12, 200 in Craven Arms sampling site locations (**Appendix 2**). The traffic population relates with that of the Highway Agency (**Appendix 3**). The population was categorised into light personal cars, light goods vehicles (LGVs: vans, minibuses, chassis cab), and heavy goods vehicles (HGVs: trucks, trailers, tractors) and represents the real time travel characteristic of the study area. The traffic counts showed traffic flows ranging from 224 vehicles per hour at the All Stretton site to 656 at the Craven Arms site. A traffic mix which differed at the various sites was observed with personal light cars (69.94%) dominating the overall traffic flow when compared to light goods vehicles (18.94%) and heavy-duty vehicles (11.60%). The significant difference in traffic flow density and fleet compositions describe the dissimilarity in the operational dynamics (driving mode) and traffic characteristics between the four site locations.

Figure 4.1 shows the traffic counts (in various fleet compositions) along the selected sampling sites of the A49 trunk road between June 2008 and April 2010.

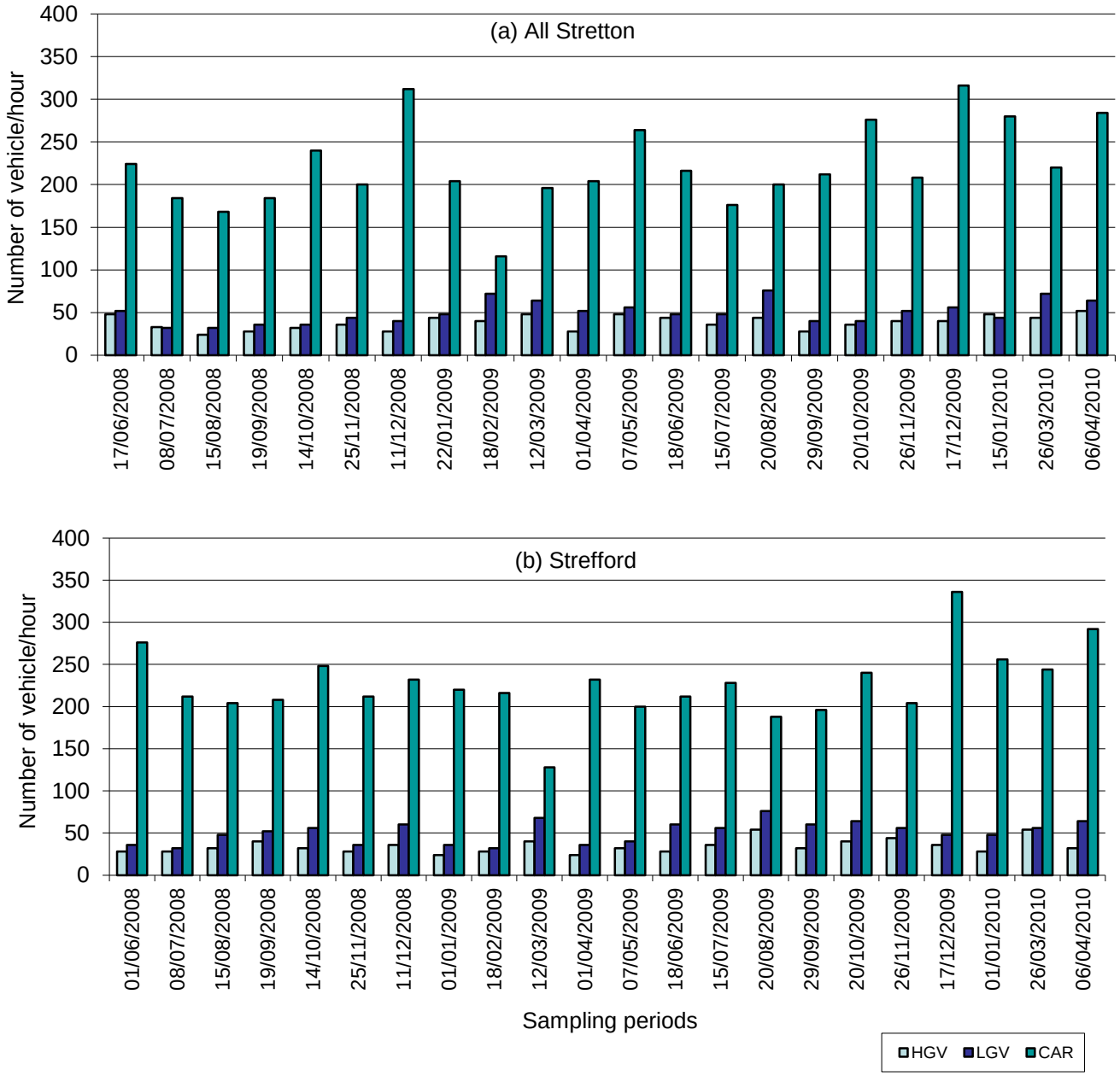


Figure 4.1: Traffic volume/hour showing vehicle fleet compositions in: (a) All Streton and (b) Strefford Site

At All Stretton, the traffic flow rate ranged between 116 and 312 representing 71.68% and a mean value of 224.55 for light personal cars, compared to LGVs that ranged from 32-76 representing 16.02% and an average value of 50.18. The range for HGVs was from

24-52, representing 12.30% and a mean value of 38.55 of the total traffic flow at the sampling site. At Strefford site location, light personal cars varied from 128 to 336 depicting 72.65% and mean value of 222.45 for personal cars, 16.33% and average of 50.91 for LGVs, and 11.02% representing mean traffic flow of 34.36 for HGVs.

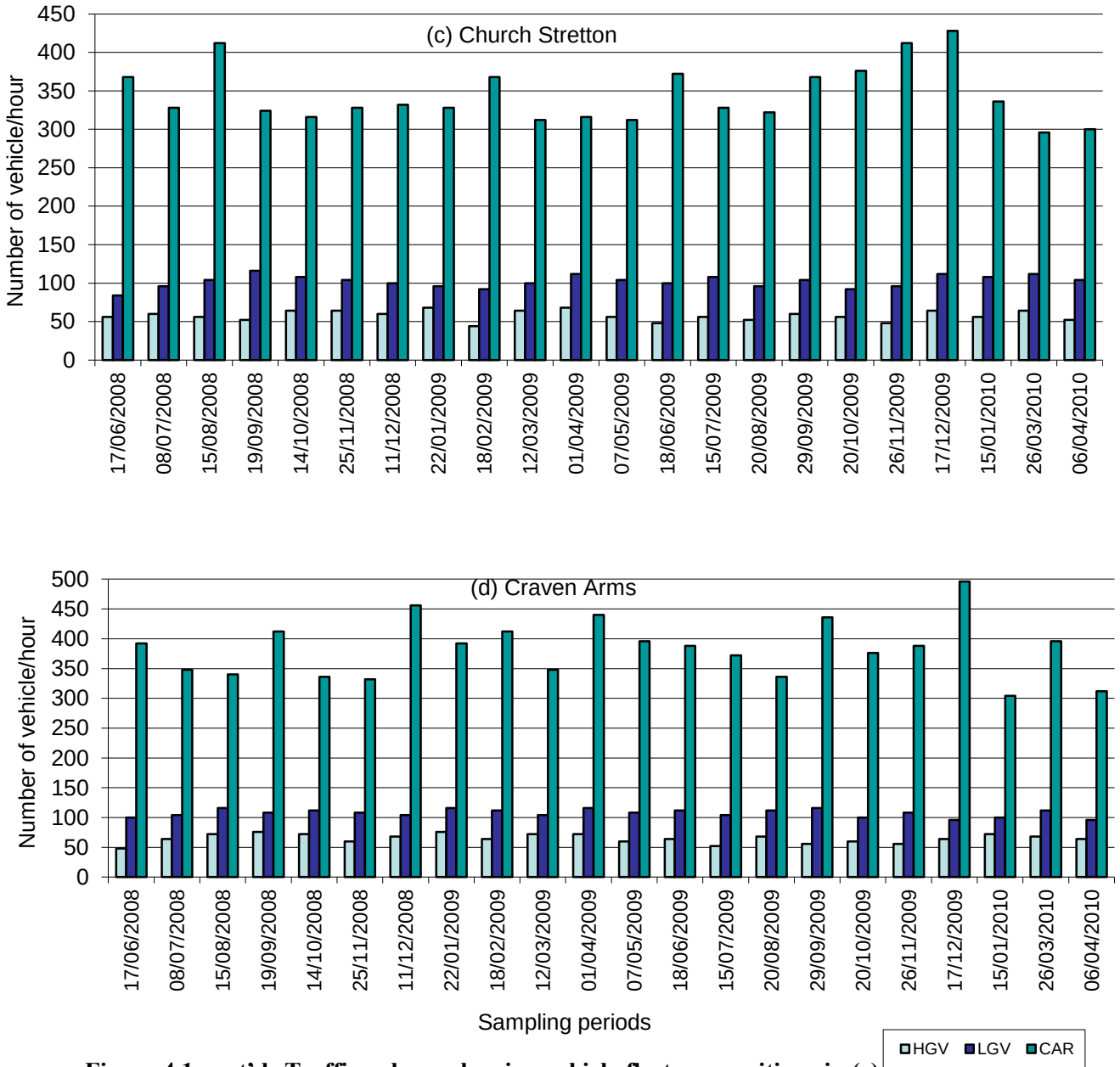


Figure 4.1 cont'd: Traffic volume showing vehicle fleet compositions in (c) Church Stretton (d) Craven Arms

At Church Stretton, the traffic flow rate ranged from 296 to 428 comprising 68.35% and mean value of 345.09 for light personal cars compared to 20.24%, representing average traffic flow of 102.18 for LGVs, and 11.42% and average value of 57.64 for HGVs. Light personal cars in Craven arms ranged from 304 to 496, which make up 68.92% and mean value of 382.18 compared to LGVs with the range of 96-116 and contributing 19.38% and mean value of 107.45, and 11.70% and average HGV flow of 64.91 of the total traffic flow in the site location. The mean traffic flow values are higher in Craven Arms and followed by Church Stretton, Strefford and All Stretton site locations representing the typical characteristic of the site locations.

4.3 Short-term tube measurements of gaseous emissions

Monitoring was carried out in two successive campaigns and thus, is presented as first and second monitoring campaigns in the following section.

First monitoring campaign

Figures 4.2-4.5 show variation in concentrations of HC and NO_2 using the short-term tubes in all four sampling sites (AS: All Stretton; ST: Strefford; CS: Church Stretton; CA: Craven Arms) in four different seasons during the first campaign.

Figure 4.2: Short-term tube mid-summer measurements for NO_2 and HC showing set limit for NO_2 concentrations during first monitoring campaign (July 8, 2008). Note: No set limits for HC regulations at present.

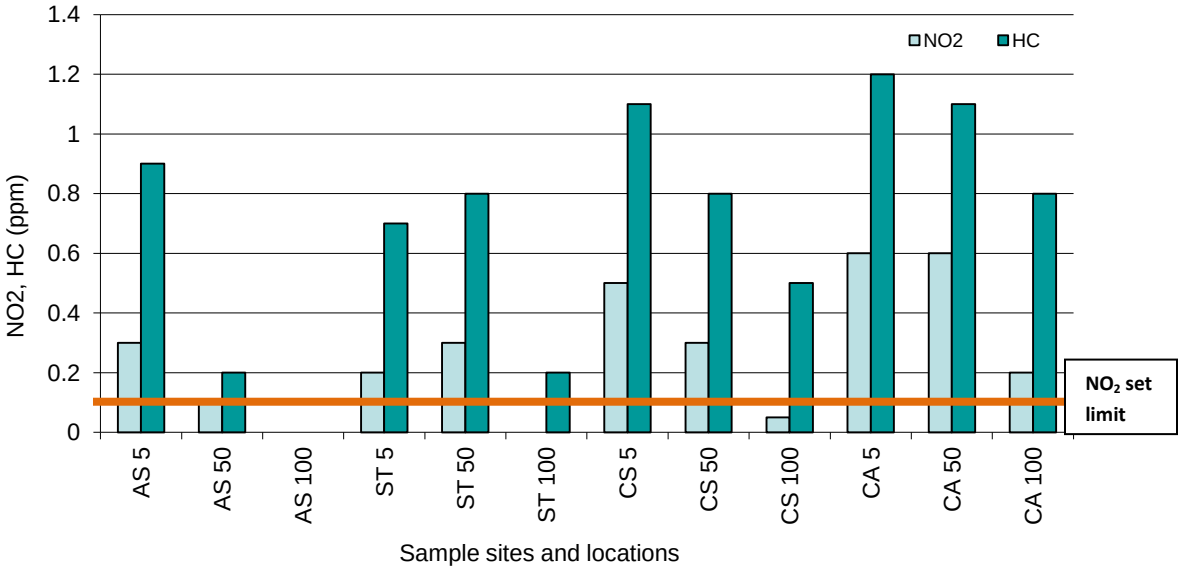


Figure 4.3: Short-term tube mid-autumn measurements for NO_2 and HC showing set limit concentrations for NO_2 during first monitoring campaign (October 14, 2008)

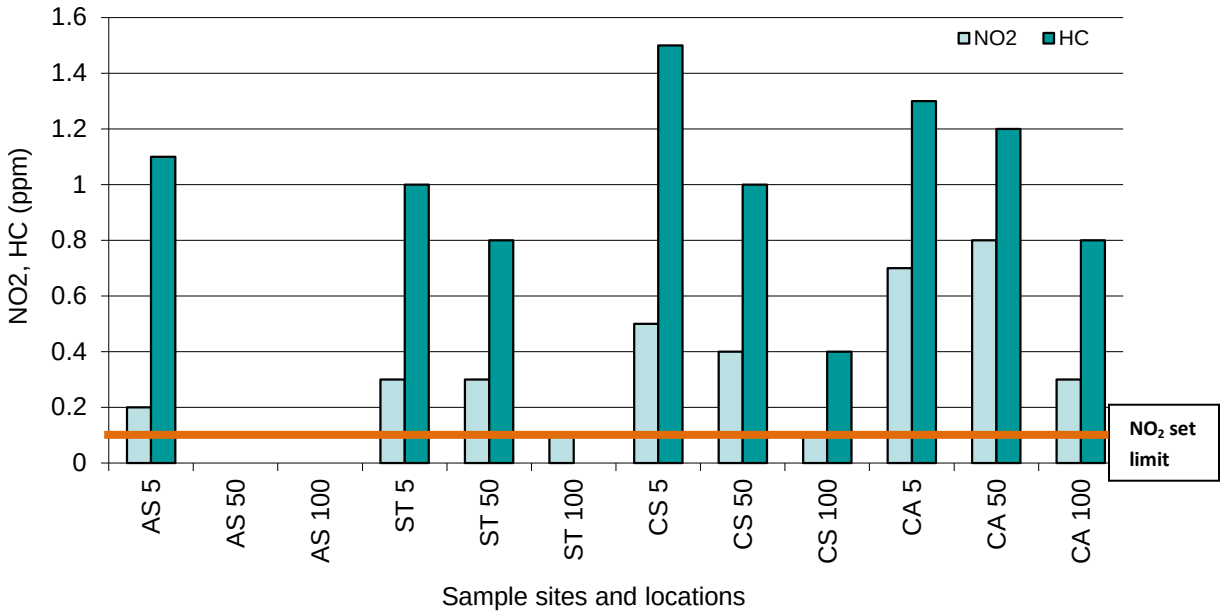


Figure 4.4: Short-term tube mid-winter measurements for NO_2 and HC showing set limit concentrations for NO2 during first monitoring campaign (January 22, 2009)

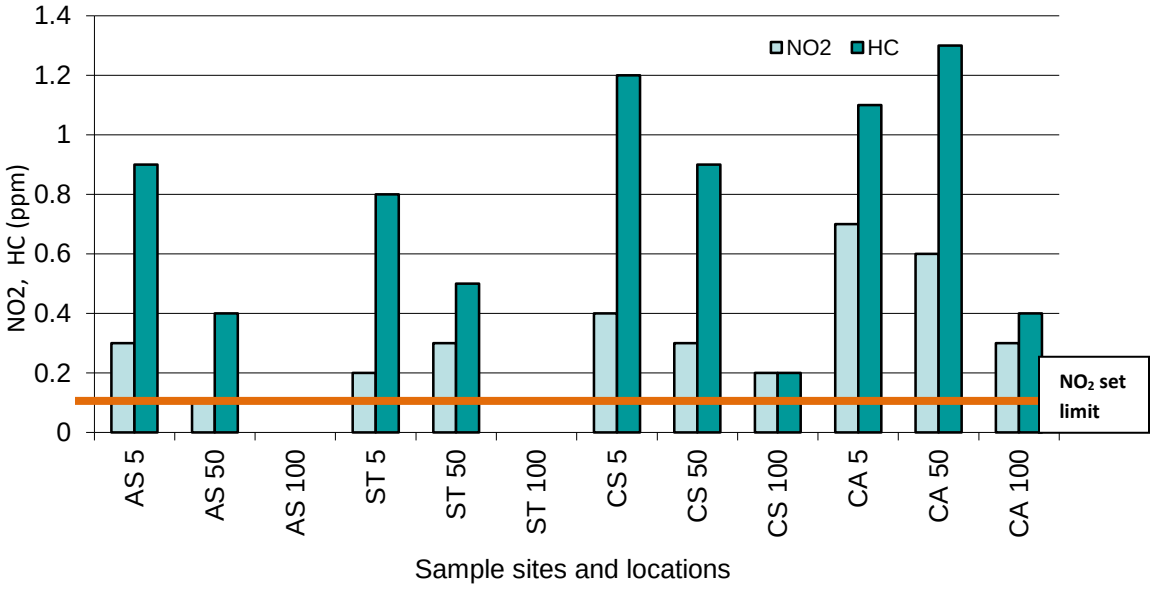


Figure 4.5: Short-term tube mid-spring measurements for NO_2 and HC showing set limit concentrations for NO_2 during first monitoring campaigns (April 1, 2009)

Second monitoring campaign

Figures 4.6-4.9 present the concentration variations for both HC and NO_2 gaseous pollutants during the second monitoring campaign in all seasons.

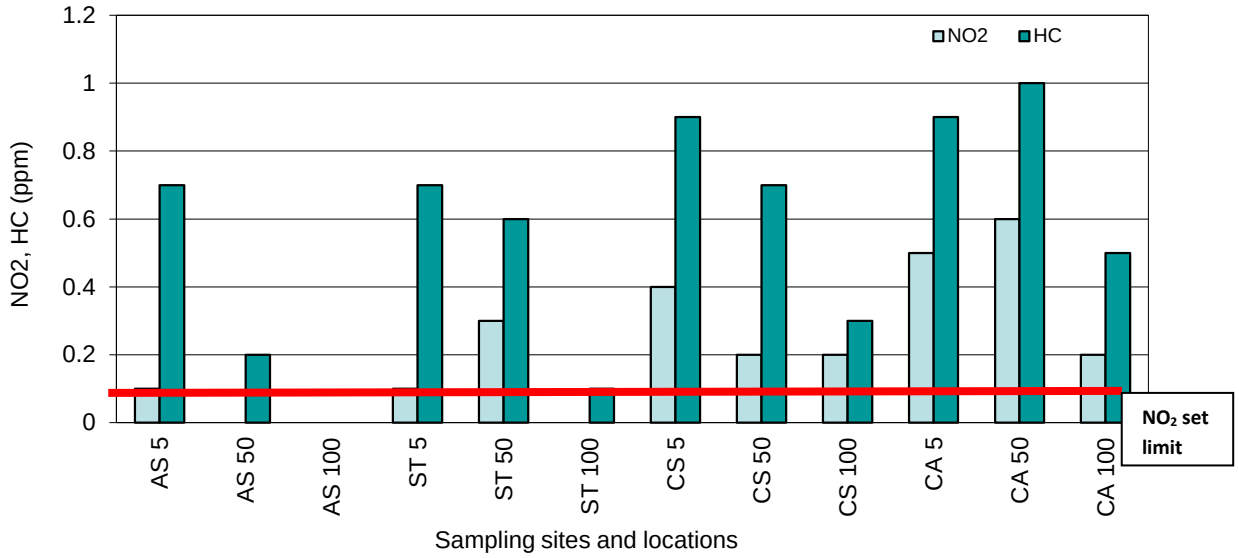


Figure 4.6: Short-term tube mid-summer measurement for NO_2 and HC showing set limit concentration for NO_2 during the second monitoring campaign (July 15, 2009)

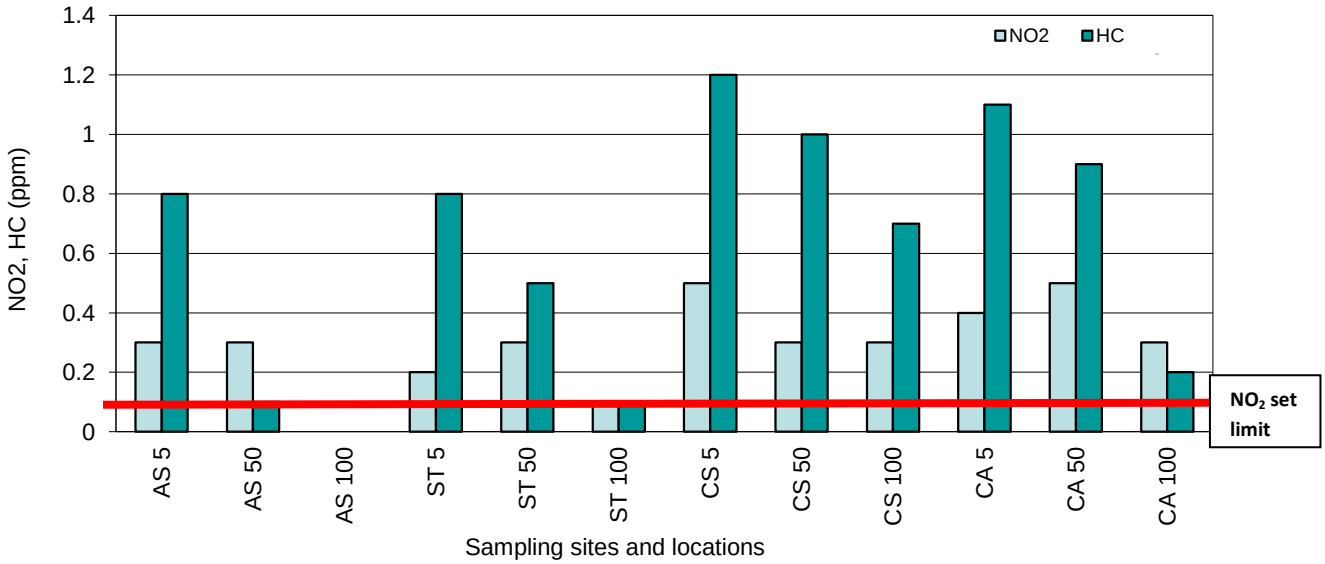


Figure 4.7: Short-term tube mid-autumn measurement for NO_2 and HC showing set limit concentration for NO_2 during the second monitoring campaign (October 20, 2009)

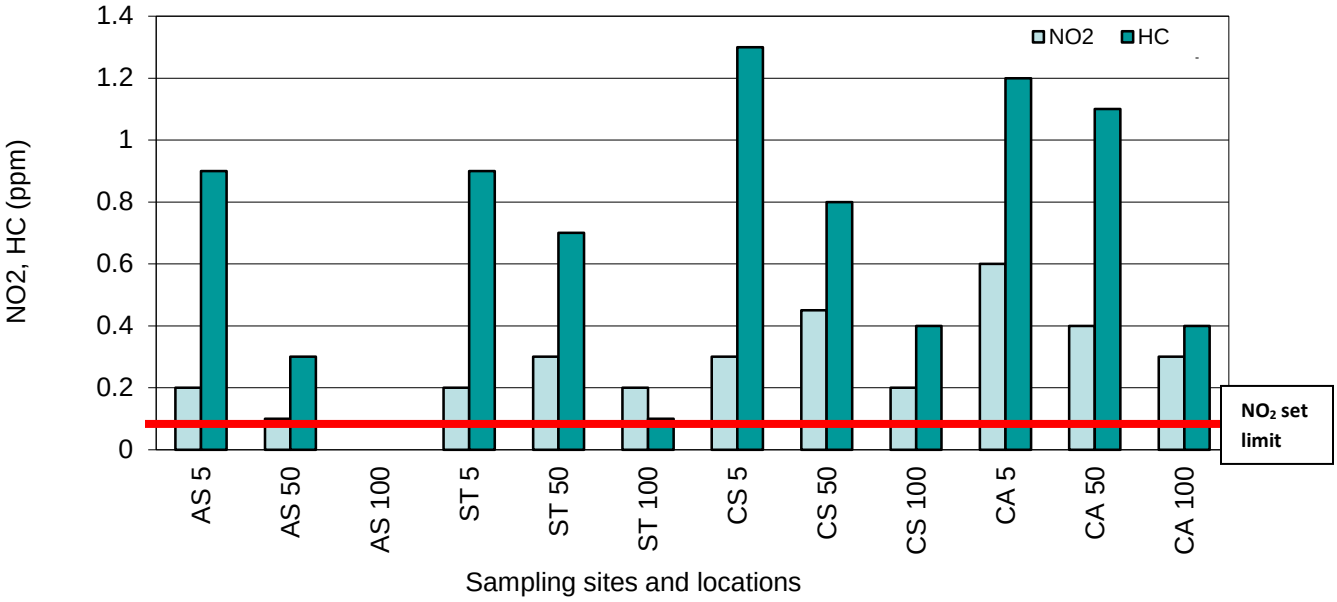


Figure 4.8: Mid-winter measurements for NO_2 and HC showing set limit concentrations for NO_2 during the second monitoring campaign (January 15, 2010).

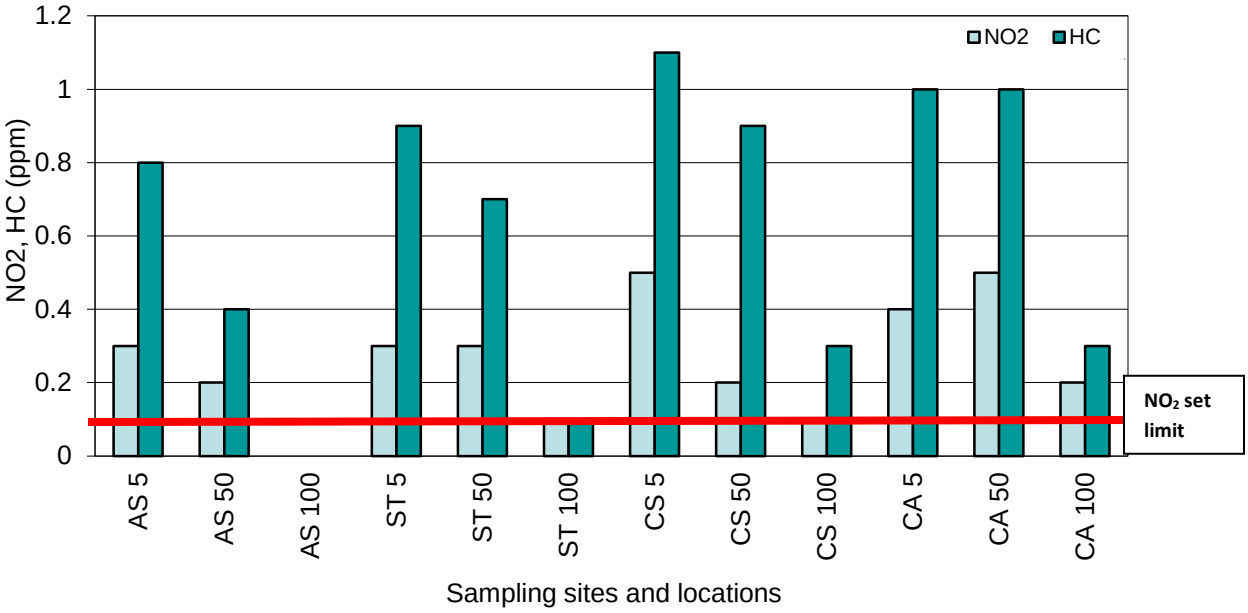


Figure 4.9: Mid-spring measurements for NO_2 and HC showing set limit concentrations for NO_2 during the second monitoring campaign (April 6, 2010)

Nitrogen dioxide

In the first monitoring campaign, concentrations were predominantly elevated at roadsides (5 m) and diminish on further progression toward other distances along each transect and at some instances merge to undetectable levels. They range from 0.03 ppm (61.61 µg/m^3) during autumn at 100 m distance from the trunk road to 0.8 ppm (1642.86 µg/m^3) during winter at the roadside (5 m from the trunk road). While the former was less than the set limit (200 µg/m^3), the latter exceeded the set limit of the UK Air Quality Objectives. The second campaign measurements show concentration range between 0.1 ppm (205.36 µg/m^3), which cuts across seasons and distances from the trunk road, and 0.6 ppm (1232 µg/m^3) at CA 50 in summer and CA 5 in winter. Both measurements show exceedances of Air Quality Objectives.

Hydrocarbon

Results showed concentrations range between 0.2 ppm in both autumn and spring and 1.5 ppm in winter. The dominant trends observed were elevated concentrations at roadside (5 m) measurements and a reciprocal decrease of concentrations with increasing distance from the trunk road, which may eventually attain background levels at further distance increment. These trends were dominant at the first monitoring campaign. In the second measurement campaign, concentrations range from 0.1 ppm in summer and autumn within 50 and 100 m distances, and 1.3 ppm in winter at roadside (5 m from the road) of Church Stretton sampling site. Similar distance-decay relationship was dominant between concentrations and distances from the trunk road as was in the first monitoring campaign. The central denominator of both campaigns is that the elevated concentrations of HC

were predominant at the sampling sites with high traffic density relative to sampling sites with less traffic counts.

4.3.1 Seasonal variations of pollutants from first and second monitoring campaigns

To compare the seasonal variations of the pollutants, pair t-Test analyses were carried out between seasons from both monitoring campaigns as shown in **Tables 4.1-4.8**.

Table 4.1: Pair t-Test analysis between NO_2 in first and second sampling campaign (mid-summer)

	NO_2*	NO_2**
Mean	0.183333333	0.216667
Variance	0.021515152	0.039697
Observations	12	12
Pearson Correlation	0.788040921	
Df	11	
P(T<=t) two-tail	0.368342595	

NO_2*: NO_2 from first monitoring campaign; NO_2: NO_2 from second monitoring campaign; p≤0.05: significantly different; p>0.05: significantly not different**

Table 4.2: Pair t-Test analysis between NO_2 in first and second sampling campaign (mid-autumn)

	NO_2*	NO_2**
Mean	0.2625	0.291666667
Variance	0.045966	0.020833333
Observations	12	12
Pearson Correlation	0.840922	
Df	11	
P(T<=t) two-tail	0.423205	

NO_2*: NO_2 from first monitoring campaign; NO_2: NO_2 from second monitoring campaign; p≤0.05: significantly different; p>0.05: significantly not different**

Table 4.3: Pair t-Test analysis between NO_2 in first and second sampling campaign (mid-winter)

	NO_2*	NO_2**
Mean	0.308333333	0.270833333
Variance	0.066287879	0.025662879
Observations	12	12
Pearson Correlation	0.855019475	
Df	11	
P(T<=t) two-tail	0.393759906	

NO_2*: NO_2 from first monitoring campaign; NO_2: NO_2 from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Table 4.4: Pair t-Test analysis between NO_2 in first and second sampling campaign (mid-spring)

	NO_2*	NO_2**
Mean	0.283333333	0.25833333
Variance	0.045151515	0.0244697
Observations	12	12
Pearson Correlation	0.82505743	
Df	11	
P(T<=t) two-tail	0.490977434	

NO_2*: NO_2 from first monitoring campaign; NO_2: NO_2 from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Table 4.5: Pair t-Test analysis between HC in first and second sampling campaign (mid-summer)

	HC*	HC**
Mean	0.533333	0.55
Variance	0.202424	0.11
Observations	12	12
Pearson Correlation	0.871196	
Df	11	
P(T<=t) two-tail	0.805568	

HC*: HC from first monitoring campaign; HC: HC from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Table 4.6: Pair t-Test analysis between HC in first and second sampling campaign (mid-autumn)

	HC*	HC**
Mean	0.6916667	0.6166667
Variance	0.1517424	0.179697
Observations	12	12
Pearson Correlation	0.8487385	
Df	11	
P(T<=t) two-tail	0.2749615	

HC*: HC from first monitoring campaign; HC: HC from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Table 4.7: Pair t-Test analysis between HC in first and second sampling campaign (mid-winter)

	HC*	HC**
Mean	0.758333333	0.675
Variance	0.284469697	0.185682
Observations	12	12
Pearson Correlation	0.956249239	
Df	11	
P(T<=t) two-tail	0.127159688	

HC*: HC from first monitoring campaign; HC: HC from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Table 4.8: Pair t-Test analysis between HC in first and second sampling campaign (mid-spring)

	HC*	HC**
Mean	0.641666667	0.625
Variance	0.206287879	0.1475
Observations	12	12
Pearson Correlation	0.962850581	
Df	11	
P(T<=t) two-tail	0.674237238	

HC*: HC from first monitoring campaign; HC: HC from second monitoring campaign;**

p≤0.05: significantly different; p>0.05: significantly not different

Results show that spatial distribution patterns of NO_2 pollutant between two corresponding seasons was not significantly different at p>0.05 while the Pearson Correlations show strong positive values between seasons. Thus, in mid-summer (P = 0.3, r^2 = 0.78), mid-autumn (P = 0.4, r^2 = 0.84), winter (P = 0.3, r^2 = 0.85), and mid-spring (P = 0.4, r^2 = 0.82). Mean concentration of NO_2* and NO_2** range from 0.18-0.30 ppm and 0.21-0.29 ppm respectively.

Pair t-Test analyses of HC concentrations was similar to NO_2 in showing no significant difference in concentrations between corresponding seasons from first and second monitoring campaigns and strong positive r^2-values: summer (P = 0.8, r^2 = 0.87), autumn (P = 0.2, r^2 = 0.84), winter (P = 0.1, r^2 = 0.95), (spring P = 0.6, r^2 = 0.96). Mean concentrations variation ranged from 0.53-0.75 ppm for HC* and 0.55-0.67 ppm for HC**. Results indicate that the trends of variation in concentrations between corresponding seasons from first and second monitoring campaigns did not differ significantly and their spatial distribution followed similar pattern irrespective of the season. The strong positive r^2-values suggest that the variables from both measurement campaigns are linearly related and the extent of such association is shown by the proximity to +1 of the r^2-values between variables from both campaigns.

4.4 Regression analyses between traffic flow and short-term measured pollutants

The relationship between traffic flow and concentration of pollutants was analysed by plotting the former (Y-axis) against the latter (X-axis) using Microsoft Excel 2010. While NO_2 concentrations between distances were statistically significant at ASE 5 (P = 0.01) and ASE 50 (P = 0.04) but insignificant between other distances at All Streton (P>0.05) **(Table 4.9a)**, the association between road traffic and NO_2 concentrations yielded positive correlation at both pair of site (ASE: R=0.64, r^2=0.42; ASW: R=0.29, r^2=0.08). For hydrocarbon, significant difference was only observed at ASE 100 (P = 0.08) and ASW 100 (P = 0.05) while positive correlation was observed at both sides of the sampling site (ASE: R=0.44, r^2=0.20; ASW: R=0.48, r^2=0.23).

Table 4.9: Regression analysis between traffic flow and measured concentrations of NO_2 and HC at all sampling sites (n = 22).

(a) All Stretton site

	NO2		HC
Sampling site	*P-value*		*P-value*
ASE 5	0.01		0.3
ASE 50	0.04		0.3
ASE 100	0.3		0.08
ASW 5	0.2		0.4
ASW 50	0.8		0.6
ASW 100	0.5		0.05

p≤0.05: significant difference; p>0.05: no significant difference.

In Strefford sampling site (**Table 4.9b)**, NO_2 concentrations was significantly different (P = 0.02) between distance at STW 5 but no significant difference (P>0.05) was found along the other sampling points at both sides of the sampling site. However, positive correlation was observed between the traffic flow and NO_2 concentrations (STE: R=0.27, r^2=0.07; STW: R=0.51, r^2=0.26). For HC, no significant difference (P>0.05) was observed for all distances but correlation coefficient show positive association between traffic flow and HC concentrations at STE (R=0.44, r^2=0.19) and STW (R=0.30, r^2=0.09).

(b) Strefford East and West

	NO2		HC
Sampling site	*P-value*		*P-value*
STE 5	0.8		0.2
STE 50	0.2		0.7
STE 100	0.5		0.1
STW 5	0.02		0.3
STW 50	0.3		0.6
STW 100	0.8		0.4

p≤0.05: significant difference; p>0.05: no significant difference.

No significant difference (p>0.05) was found between distance for both NO_2 and HC concentrations at Church Stretton pair of sampling site (**Table 4.9c**). However, regression analysis show positive correlation between traffic flow and NO_2 at CSE (R=0.28, r^2=0.08) and CSW (R=0.22, r^2=0.05) as well as between traffic flow and HC at CSE (R=0.22, r^2=0.05) and CSW (R=0.51, r^2=0.26).

(c) Church Stretton East and West

	NO2	HC
Sampling site	*P-value*	*P-value*
CSE 5	0.5	0.4
CSE 50	0.6	0.5
CSE 100	0.8	0.7
CSW 5	0.4	0.1
CSW 50	0.5	0.7
CSW 100	0.8	0.06

p≤0.05: significant difference; p>0.05: no significant difference.

For both NO_2 and HC concentrations, no significant difference (P>0.05) was found between distance at both Craven Arms East and West while correlation analysis produced positive association between traffic flow and concentrations (**Table 4.9d**). Both trends are similar to those obtained from Church Stretton sampling site and therefore tend to relate to a common factor.

(d) Craven Arms East and West

	NO2		HC
Sampling site	*P-value*		*P-value*
CAE 5	0.4		0.6
CAE 50	0.2		0.3
CAE 100	0.6		0.9
CAW 50	0.5		0.7
CAW 50	0.3		0.7
CAW 100	0.3		0.8

p≤0.05: significant difference; p>0.05: no significant difference.

4.4.1 Relating meteorological parameters with NO_2 and HC

The importance of regression analyses was to gain deeper understanding of the dependence of air quality on the emission levels of the measured pollutants in the study area. It aims to establish the relationship between meteorological parameters and NO_2 and HC. The analysis was restricted to All Stretton and Strefford sampling sites as shown in **Table 4.10 (a-c)** because of missing meteorological data from Church Stretton and Craven Arms. The closer *R* and r^2 are to one, the higher the correlation of meteorological parameters to the pollutants.

When wind speed (vertical axis) was plotted against the concentration of the pollutants on the horizontal axis, NO_2 was found statistically different at ASE 5 ($P<0.0001$), ASW 5 ($P\leq0.05$) and ASW 50 ($P\leq0.05$) (**Table 4.10a**). No significant difference was observed at ASE 50, ASE 100, and ASW 100. However, the association between wind speed and concentrations of NO_2 showed positive *R* (0.83) and $\boldsymbol{r^2}$ (0.69) values, indicating a strong relationship between wind speed and the distribution of pollutants. For HC, the statistical differences were significant ($p\leq0.05$) at ASW 5 and ASW 50 sample points but

insignificant at ASE sample points as well as at ASW 100 while *R* and r^2 values of 0.81 and 0.66 respectively were observed, signifying strong relationship between wind speed and the distribution of HC pollutant.

Wind speed plotted against NO_2 concentrations at both pair of Strefford sampling site produced significant difference only at STW 100 but with positive *R* and r^2 values of 0.77 and 0.60 respectively (**Table 4.10a**).

Table 4.10a: Relating wind speed with NO_2 and HC concentrations

NO2					HC			
Site location	*P-value*		*Site location*	*P-value*	*Site location*	*P-value*	*Site location*	*P-value*
ASE 5	***		STE 5	ns	ASE 5	ns	STE 5	ns
ASE 50	ns		STE 50	ns	ASE 50	ns	STE 50	ns
ASE 100	ns		STE 100	ns	ASE 100	ns	STE 100	ns
ASW 5	*		STW 5	ns	ASW 5	*	STW 5	ns
ASW 50	*		STW 50	ns	ASW 50	*	STW 50	ns
ASW 100	ns		STW 100	*	ASW 100	ns	STW 100	ns

ns: not significant difference (p>0.05); *: significant difference (p≤0.05), *= (p<0.0001)**

The relationship between temperature (dependent variable) and the pollutants (independent variables) produced significant differences ($P \leq 0.05$) at ASE 5 and ASE 50 for NO_2, and for HC at ASW 5 and exhibited strong positive *R* and r^2 values. However, the relationship show low r^2 value at Strefford sampling site (**Table 4.10b)**.

Table 4.10b: Relating temperature with NO_2 and HC concentration

NO2					HC			
Site location	*P-value*		*Site location*	*P-value*	*Site location*	*P-value*	*Site location*	*P-value*
ASE 5	*		STE 5	ns	ASE 5	ns	STE 5	ns
ASE 50	*		STE 50	ns	ASE 50	ns	STE 50	ns
ASE 100	ns		STE 100	ns	ASE 100	ns	STE 100	ns
ASW 5	ns		STW 5	ns	ASW 5	*	STW 5	ns
ASW 50	ns		STW 50	ns	ASW 50	ns	STW 50	ns
ASW 100	ns		STW 100	ns	ASW 100	ns	STW 100	ns

ns: no significant difference (p>0.05); *: significant difference (p≤0.05).

From **Table 4.10c**, the difference between the pollutants was statistically significant (p≤0.05) at ASE 5, ASW 5 and STW 5 for NO_2 and ASE 50, ASE 100, ASW 5, ASW 50 and STE 5 for HC. Their respective *R* (0.80 and 0.85) and r^2 values (64 and 73) for NO_2, *R* (0.89 and 0.92) and r^2 (0.80 to 0.86) values for HC suggest a strong influence of relative humidity on the spatial distribution of both pollutants.

Table 4.10c: Relating relative humidity with NO_2 and HC concentration

NO2					HC			
Site location	*P-value*		*Site location*	*P-value*	*Site location*	*P-value*	*Site location*	*P-value*
ASE 5	*		STE 5	ns	ASE 5	ns	STE 5	*
ASE 50	ns		STE 50	ns	ASE 50	*	STE 50	ns
ASE 100	ns		STE 100	ns	ASE 100	*	STE 100	ns
ASW 5	*		STW 5	*	ASW 5	*	STW 5	ns
ASW 50	ns		STW 50	ns	ASW 50	*	STW 50	ns
ASW 100	ns		STW 100	ns	ASW 100	ns	STW 100	ns

ns: not significant difference (p>0.05); *: significant difference (p≤0.05).

4.5 Seasonal variation of NO_2 and SO_2 from passive (diffusion) tube measurements

Despite SO_2 was not detected using the short-term tube; the three-weekly exposure period using passive tube technique detected this pollutant. At three-weekly exposure period, it is apparent that both gaseous pollutant tubes were subject to various environmental influences. In the light of this, it was apt to investigate the differences between both pollutants and determine if their statistical difference was significant by applying a Paired t-Test analysis.

Winter measurement of NO_2 and SO_2

Figure 4.2 demonstrates the three-weekly measurement of the mean concentrations of NO_2 and SO_2 in mid-winter season. Concentrations of pollutants (on vertical axis) against sample locations, representing distances from the road, show maximum concentrations for both pollutants were obtained at the roadsides and their values corresponded to the localised traffic characteristics of the sampling sites. As shown in **Figure 4.10**, there was no record of exceedance of concentrations for SO_2 in contrast to NO_2 with predominant exceedances of the guidance limit at 5 and 50 m distances.

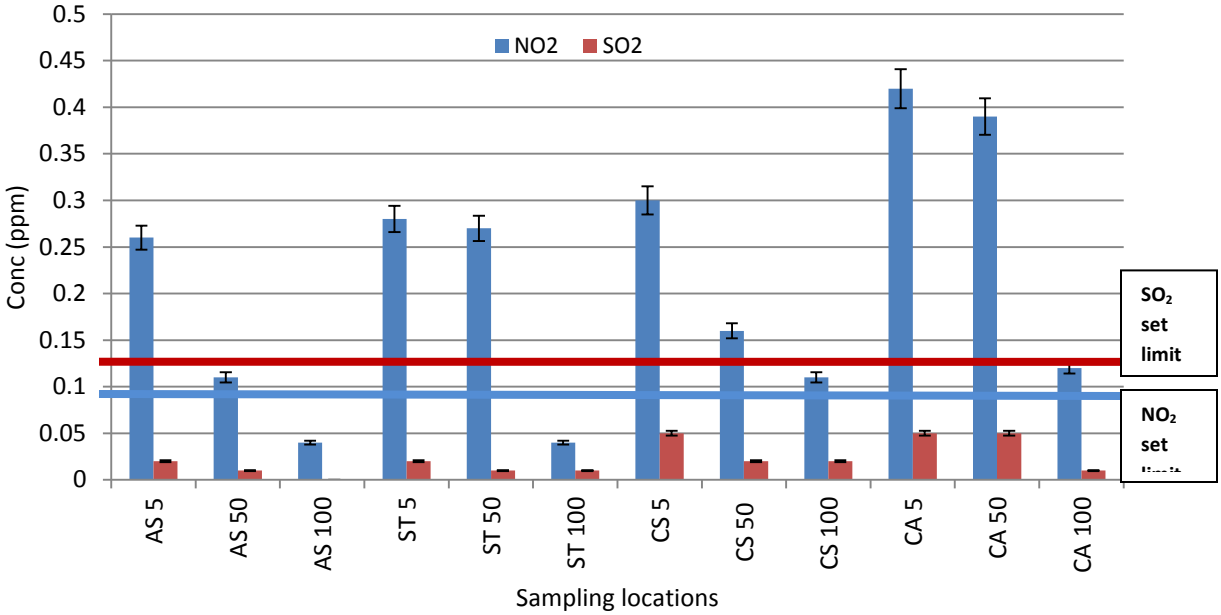


Figure 4.10: Three weekly passive diffusion tube measurements of NO_2 and SO_2 (January 7-28, 2009) showing guidance limits.

Spring measurement of NO_2 and SO_2

Figure 4.11 presents the three-weekly mean concentrations of NO_2 and SO_2 in mid-spring season (April 6-27, 2009). The results follow similar trends in showing reciprocal decrease in concentration with increasing distance from the trunk road. Nitrogen dioxide concentrations range from 0.33 ppm (677.67 $\mu g/m^3$) at the roadside of Craven Arms to 0.01 ppm (20.53 $\mu g/m^3$) obtained at 100 m distance of Strefford site location. While the concentrations values reflect the characteristic traffic flow of the sites, it is important to note that concentrations of NO_2 predominantly exceeded guidance level up to 50 m from the trunk road while there was no occurrence of exceedance of guidance limit for SO_2 concentrations as shown in **Figure 4.11**. The error bars indicate the standard deviation of concentration from the mean concentration. Standard deviations lower than the mean

values suggest that the trend of variations of the pollutants are more precise (small error bars) in contrast to those with higher standard deviation (large error bars).

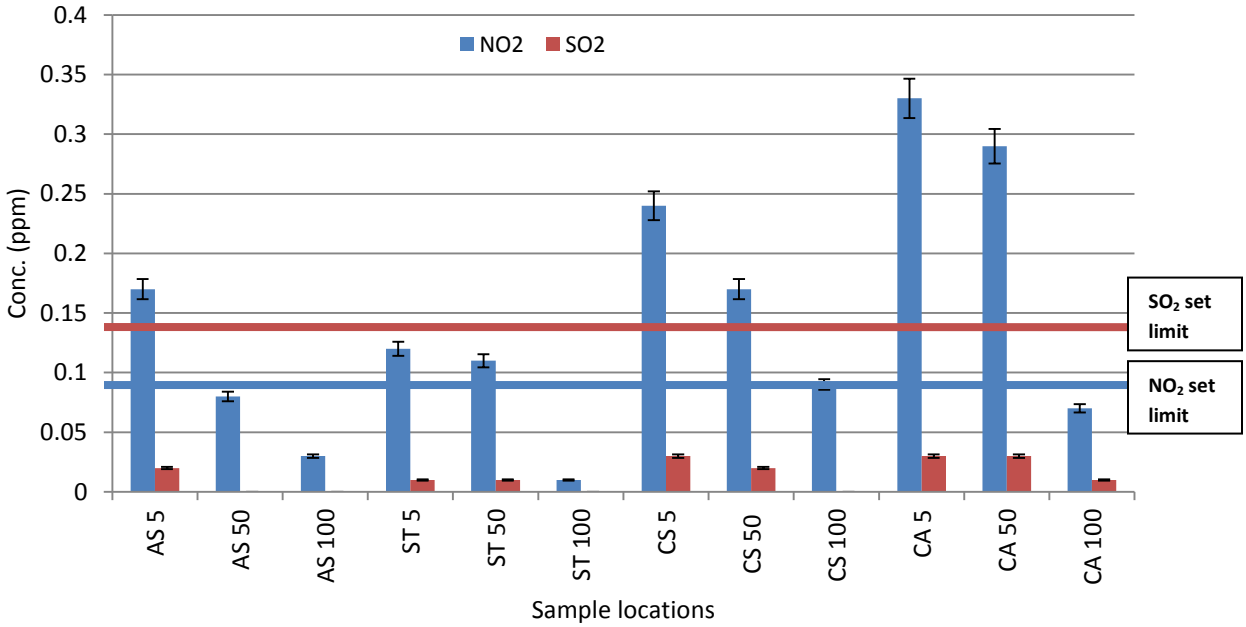


Figure 4.11: Three weekly passive diffusion tube measurements of NO_2 and SO_2 (April 6-27, 2009) showing guidance limits.

Summer measurement of NO_2 and SO_2

Figure 4.12 illustrates the three weekly passive measurements of NO_2 and SO_2 during mid-summer season. Results show a consistent gradient decline of the pollutants with increasing distance from the trunk road in all sites, similar to the previous seasonal measurements. Concentrations for NO_2 exceeeded the guidance set limit (200 µg/m^3) up to 100 m distance in Church stretton and Craven Arms sampling sites while no exceedance of concentrations was found for SO_2 measurements.

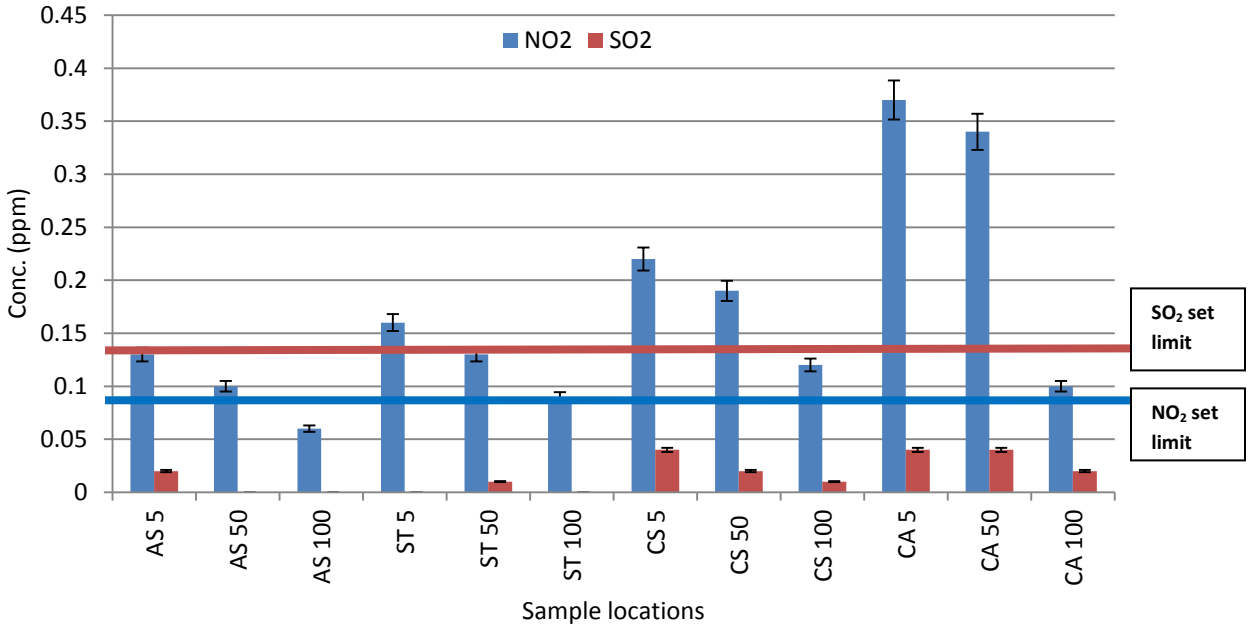


Figure 4.12: Three weekly passive diffusion tube measurements of NO_2 and SO_2 (July 10-30, 2009) showing guidance limits.

Autumn measurement of NO_2 and SO_2

Mid-autumn measurements of NO_2 and SO_2 show maximum concentrations at roadsides but diminish with increasing distance from the trunk road. However, NO_2 concentrations at 50 m distance location exceeded the roadside concentrations at Strefford site location (**Figure 4.13**). This distance location corresponds to the farm access road junction that serves as both entry and exiting point for traffic (see section 3.1.2). Concentrations of NO_2 exceeded the set limit mainly at 5 and 50 m distances from the road and extended to 100 m at Church Stretton sampling site. However, SO_2 concentrations were well below the guidance level at all four sampling sites (**Figure 4.13**). Descriptive analyses between each pair of the sampling sites show the maximum and minimum concentrations in each sampling site in addition to the degree of deviation of concentrations from their respective mean values. While high standard deviations (indicated by large error bars)

exceeded the mean values of the pollutants, others did not exceed their mean values as indicated by small error bars.

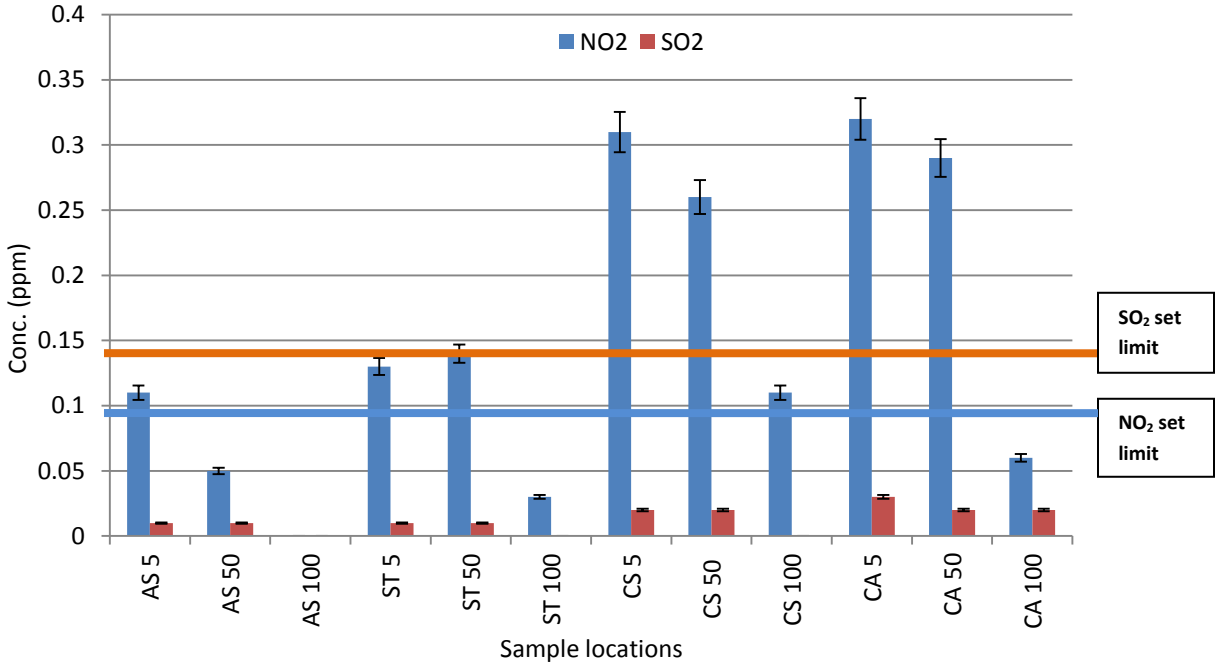


Figure 4.13: Three weekly passive diffusion tube measurements of NO_2 and SO_2 (October 8-28, 2008) showing their guidance limits.

4.5.1 Statistical analyses for NO_2 and SO_2 spatial and temporal variations

Table 4.11a presents the paired t-Test analysis between mid-winter (NO_2^{+}) and mid-spring (NO_2^{++}) measurements. Results show higher mean concentrations for NO_2 (0.208 ppm (418.93 µg/m^3)) in mid-winter than NO_2 (0.143 ppm (293.66 µg/m^3) in mid-spring, an indication that both measurements exceeded the set limit (200 µg/m^3). The difference between both seasons were statistically significant (P = 0.001) with a strong positive correlation (0.91) which indicates a linear association between both seasons. **Table 4.11b** compares mid-winter with mid-spring concentrations of SO_2 using pair t-Test analysis. Mean concentration between both seasons range from 0.023 ppm (65.71 µg/m^3) and

0.013 ppm (37.14 μg/m^3) and were both well below the set limit for SO_2. Their difference was statistically significant (P = 0.004) and yieded a strong positive r^2 value (0.87).

Table 4.11a: Pair t-Test analysis between mid-winter and mid-spring NO_2 concentrations

	$NO2^+$	$NO2^{++}$
Mean	0.208333	0.1425
Variance	0.016724	0.010148
Observations	12	12
Pearson Correlation	0.913111	
Df	11	
P(T<=t) two-tail	0.001734	

Significant: p≤0.05; Not significant: p>0.05. Note: NO_2^+: Mid-winter measurement; NO_2^{++}: Mid-spring measurement

Table 4.11b: Pair t-Test analysis between mid-winter and mid-spring SO_2 concentrations

	$SO2^+$	$SO2^{++}$
Mean	0.0225	0.013333
Variance	0.000311	0.000152
Observations	12	12
Pearson Correlation	0.878951	
Df	11	
P(T<=t) two-tail	0.00474	

Significant: p≤0.05; Not significant: p>0.05. Note: SO_2^+: Mid-winter measurement; SO_2^{++}: Mid-spring measurement

Between mid-winter and mid-summer, NO_2 produced mean concentrations of 0.208 ppm (427.14 μg/m^3) in mid-winter and 0.168 ppm (345 μg/m^3) in mid-summer. Both measurements exceeded the set limit and the difference between them was significant (P = 0.05) and both variables were linearly related at r^2 = 0.87 (**Table 4.12a**). For SO_2, the mean concentrations vary from 0.017 ppm (48.57 μg/m^3) and 0.023 ppm (65.71 μg/m^3).

The difference in concentrations between mid-winter and mid-summer was statistically significant (P = 0.02) and produced a strong positive Pearson Correlation (0.89) (**Table 4.12b**).

Table 4.12a: Pair t-Test analysis between mid-winter and mid-summer NO_2 concentrations

	NO2^	NO2^^
Mean	0.208333	0.1675
Variance	0.016724	0.00962
Observations	12	12
Pearson Correlation	0.871147	
Df	11	
P(T<=t) two-tail	0.050675	

Significant: p≤0.05; Not significant: p>0.05. Note: NO_2^: Mid-winter measurements; NO_2^^: Mid-summer measurements

Table 4.12b: Pair t-Test analysis between mid-winter and mid-summer SO_2 concentrations

	SO2^	SO2^^
Mean	0.0225	0.016667
Variance	0.000311	0.000261
Observations	12	12
Pearson Correlation	0.893592	
Df	11	
P(T<=t) two-tail	0.027076	

Significant: p≤0.05; Not significant: p>0.05. Note: SO_2^: Mid-winter measurements; SO_2^^: Mid-summer measurements

Between mid-winter and mid-autumn, mean concentrations range between 0.208 ppm (427.14 μg/m^3) and 0.150 ppm (310.08 μg/m^3) in mid-winter and mid-autumn respectively. Both measurements exceeded the set limit for NO_2. The seasonal difference was statistically significant (P = 0.02) and the relationship between variables from both seasons show a strong positive Pearson Correlation (0.81) (**Table 4.13a**). The mean

concentrations for SO_2 range between 0.022 ppm (65.71 μg/m^3) and 0.012 ppm (37.14 μg/m^3) between mid-winter and mid-autumn respectively (**Table 4.13b**). The difference between both seasonal concentrations was statistically different (P = 0.02) and show a strong positive Pearson Correlation (0.70).

Table 4.13a: Pair t-Test analysis between mid-winter and mid-autumn NO_2 concentrations

	NO2[a]	NO2[b]
Mean	0.208333	0.150833
Variance	0.016724	0.013172
Observations	12	12
Pearson Correlation	0.819632	
Df	11	
P(T<=t) two-tail	0.021799	

Significant: p≤0.05; Not significant: p>0.05. Note: NO_2[a]: Mid-winter measurements and NO_2[b]: Mid-autumn measurements

Table 4.13b: Pair t-Test analysis between mid-winter and mid-autumn SO_2 concentrations

	SO2[a]	SO2[b]
Mean	0.0225	0.0125
Variance	0.000311	9.32E-05
Observations	12	12
Pearson Correlation	0.70717	
Df	11	
P(T<=t) two-tail	0.020363	

Significant: p≤0.05; Not significant: p>0.05. Note: SO_2[a]: Mid-winter measurements and SO_2[b]: Mid-autumn measurements

4.6 Elemental analysis of hazel leaf and ryegrass samples using XRF

The sensitivity of plants to heavy metal pollution differs significantly. Because heavy metals present in atmospheric dust particles are deposited on the leaves as well as other plant surfaces, washed powdered hazel leaf (***Corylus avellana***) and rye grass (***Lolium perenne***) materials were analysed for heavy metal contents using XRF following the procedures described in section 3.4.1.

4.6.1 Hazel leaf in mid-spring season

The XRF analysis of mid-spring ground loose hazel leaf sample show the presence of Mg, Ca, Ti, Cr, As, Mn, Fe, Ni, Cu, Zn, Si, Na, Se, Sb, S, P, K and Pb. Some of these elements were examined because of their toxicity and/or direct association with motor vehicle emissions. **Figure 4.14a** presents the relationship between concentration values of the elements and the trend of their spatial distribution during the mid-spring sampling period.

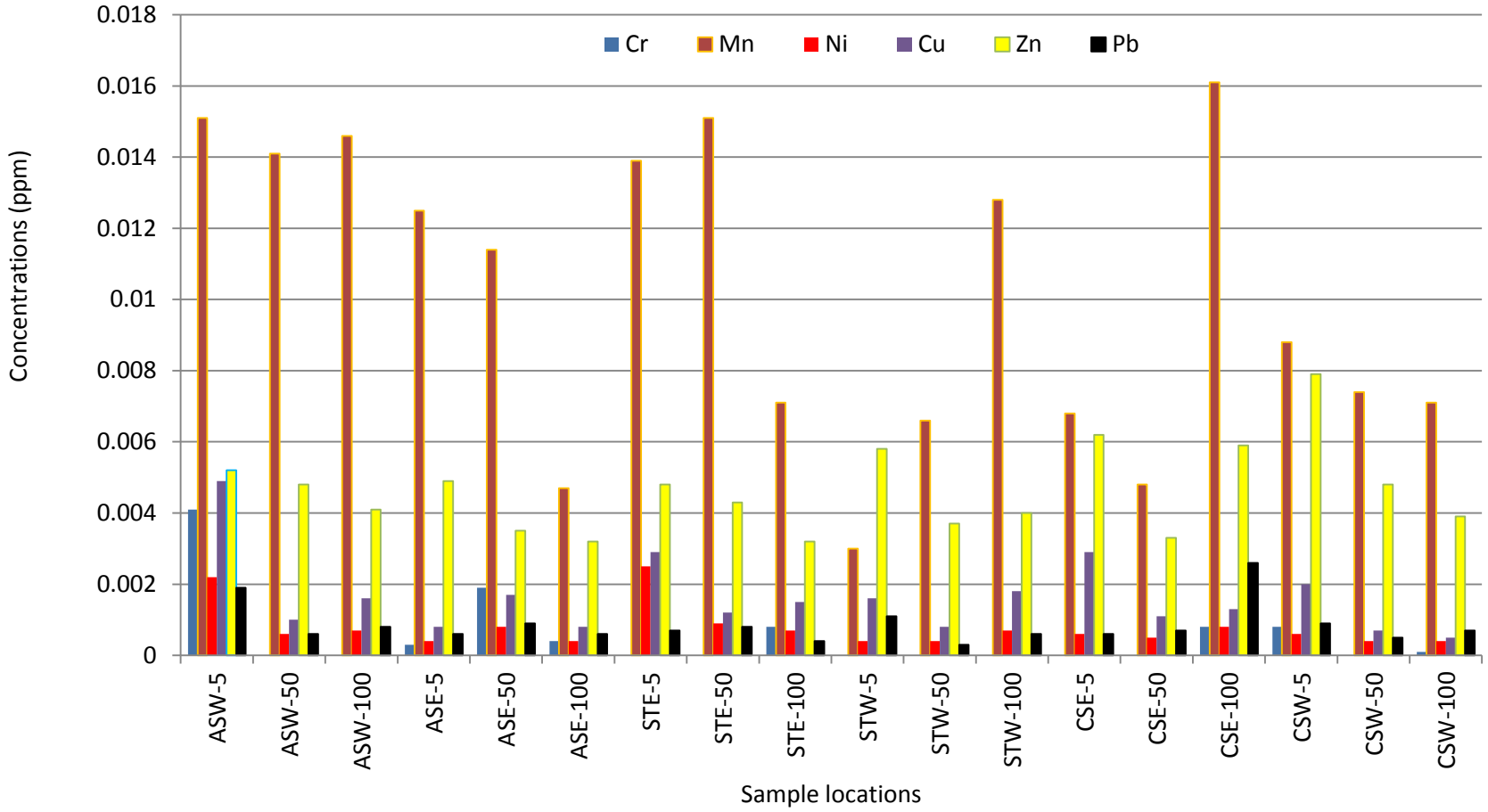


Figure 4.14a: Mid-spring elemental concentrations of hazel leaf sample (06.04.10)

Statistical analysis was conducted to determine the emission distribution between data points. It was observed that mean concentrations and standard deviations differed in both elements and sampling sites, as indicated by the error bars. **Table 4.14** shows the correlation between pair of elements of the overall elemental profile. This is because the sources of the elements (major or minor) may include anthropogenic activities, particularly traffic. However, the relevance of such association is particularly limited to Pb, Cu, Zn, Ni, Mn, Cr, Ti, and As since they are more likely signatures of anthropogenic origins.

Table 4.14: Correlation between elemental concentrations in hazel leaf sample (06.04.10)

	Mg	*Al*	*Ca*	*Ti*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*As*	*Pb*
Mg	1											
Al	0.960586	1										
Ca	0.848155	0.886599	1									
Ti	0.882577	0.965393	0.872607	1								
Cr	0.852546	0.82008	0.644068	0.754825	1							
Mn	0.868706	0.867559	0.747985	0.826028	0.818238	1						
Fe	0.929658	0.989976	0.86731	0.986742	0.803539	0.84901	1					
Ni	0.658102	0.776128	0.852694	0.745791	0.517397	0.629465	0.753978	1				
Cu	0.823901	0.830557	0.838341	0.767672	0.694174	0.663028	0.82044	0.784689	1			
Zn	0.723812	0.814565	0.785329	0.779433	0.658225	0.675207	0.82116	0.853817	0.872864	1		
As	-0.07717	-0.04078	-0.14239	0.006352	-0.15152	0.094048	-0.01327	-0.17811	-0.1135	-0.12011	1	
Pb	0.504471	0.549171	0.370625	0.535989	0.545988	0.778933	0.560952	0.344359	0.398217	0.475207	0.444895	1

4.6.2 Hazel leaf in mid-summer season

The XRF analysis of loose powder sample of hazel leaf yielded Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb. Concentration values were compared amongst the elements by

plotting the former (vertical axis) against the latter (horizontal axis) and the trend of concentration distributions tend to be similar to the mid-spring season (**Figure 4.14b**).

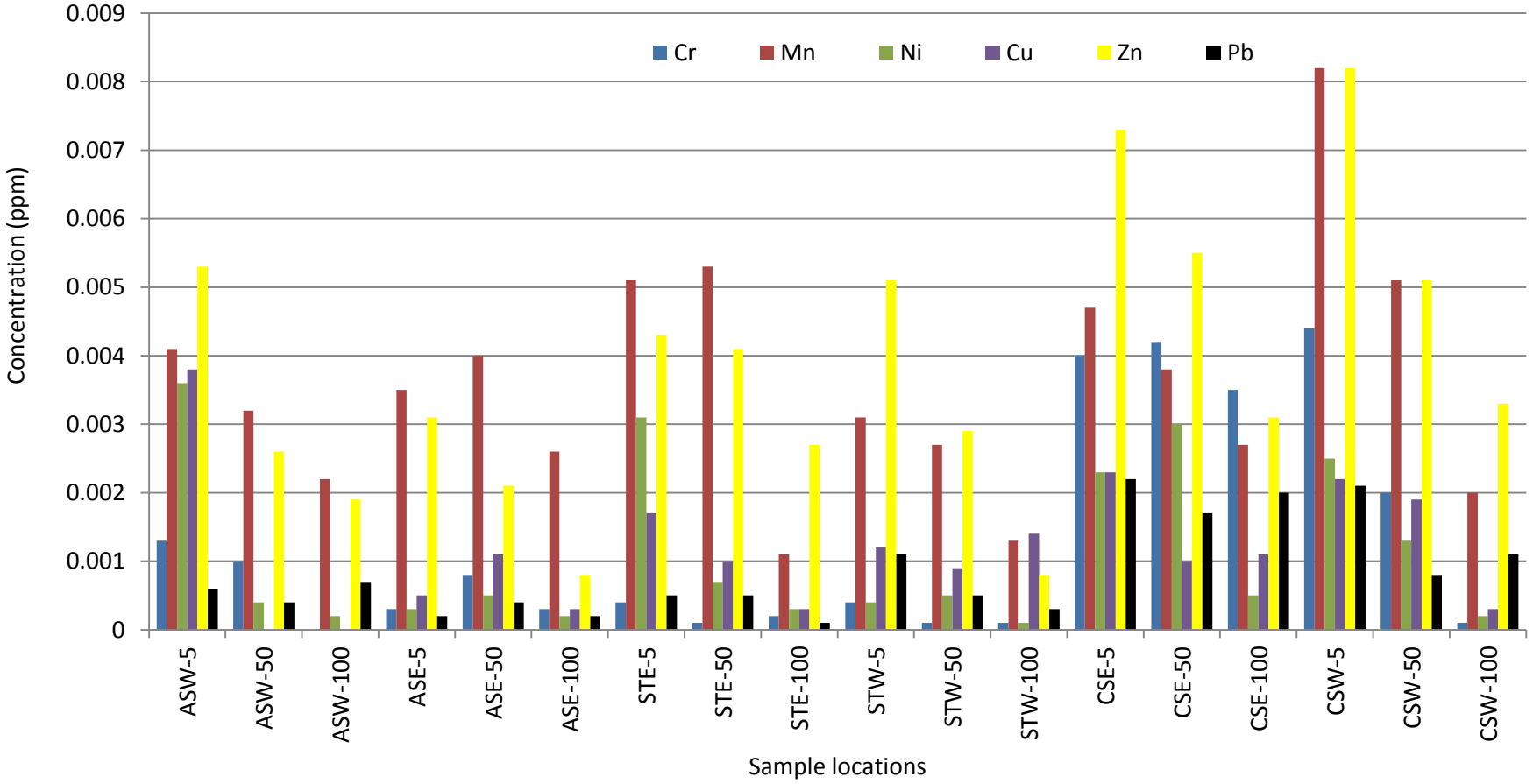


Figure 4.14b: Mid-summer elemental concentrations of hazel leaf sample (15.07.09)

Two-Factor Anova analysis, significant difference was observed between elements at the three site pairs (P = 0.008). **Table 4.15** shows that all the elements exhibited positive relationships between individual elements with each other as indicated by the correlation values. This suggests a possible common source between each pair of metals. Iron and Fe particularly displayed a very strong association considering their very high correlation coefficient while Pb and Ni exhibited low correlation coefficient. Again, the relevance of such association is particularly limited to Pb, Cu, Zn, Ni, Mn, and Cr since they are likely to be of anthropogenic origins.

Table 4.15: Correlation between elemental concentrations in hazel leaf sample (15.07.2009)

	Al	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*
Al	1							
Cr	0.818928	1						
Mn	0.865074	0.816245	1					
Fe	0.99005	0.803404	0.846703	1				
Ni	0.770092	0.510537	0.621714	0.746701	1			
Cu	0.826875	0.695608	0.65674	0.812809	0.779973	1		
Zn	0.809232	0.653945	0.668226	0.815459	0.849885	0.871287	1	
Pb	0.546821	0.543201	0.778641	0.559799	0.338725	0.395219	0.471638	1

4.6.3 Ryegrass in mid-spring season

Procedures for ryegrass sample collection and subsequent laboratory preparations are as described in section 3.4.1. Unlike the hazel sampling, ryegrass sample collection took place at all four sites. However, collection periods of ryegrass samples were the same as those of hazel leaf. Loose powder of of washed ryegrass samples were analysed by XRF. Results show the elemental profiling of Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Si, and Pb whose detection differed quantitatively with season and sampling sites. Elemental

concentrations were dominant at Craven Arms and subsequently at the Church Stretton pairs of sampling sites thus reflecting the traffic flow differential between the site locations. When concentrations of the elements were plotted against the elements, it was observed that mean values of Ca, Mg, Al, and Fe were detected in different order of magnitude at the four pairs of sampling sites (**Figure 4.15a**).

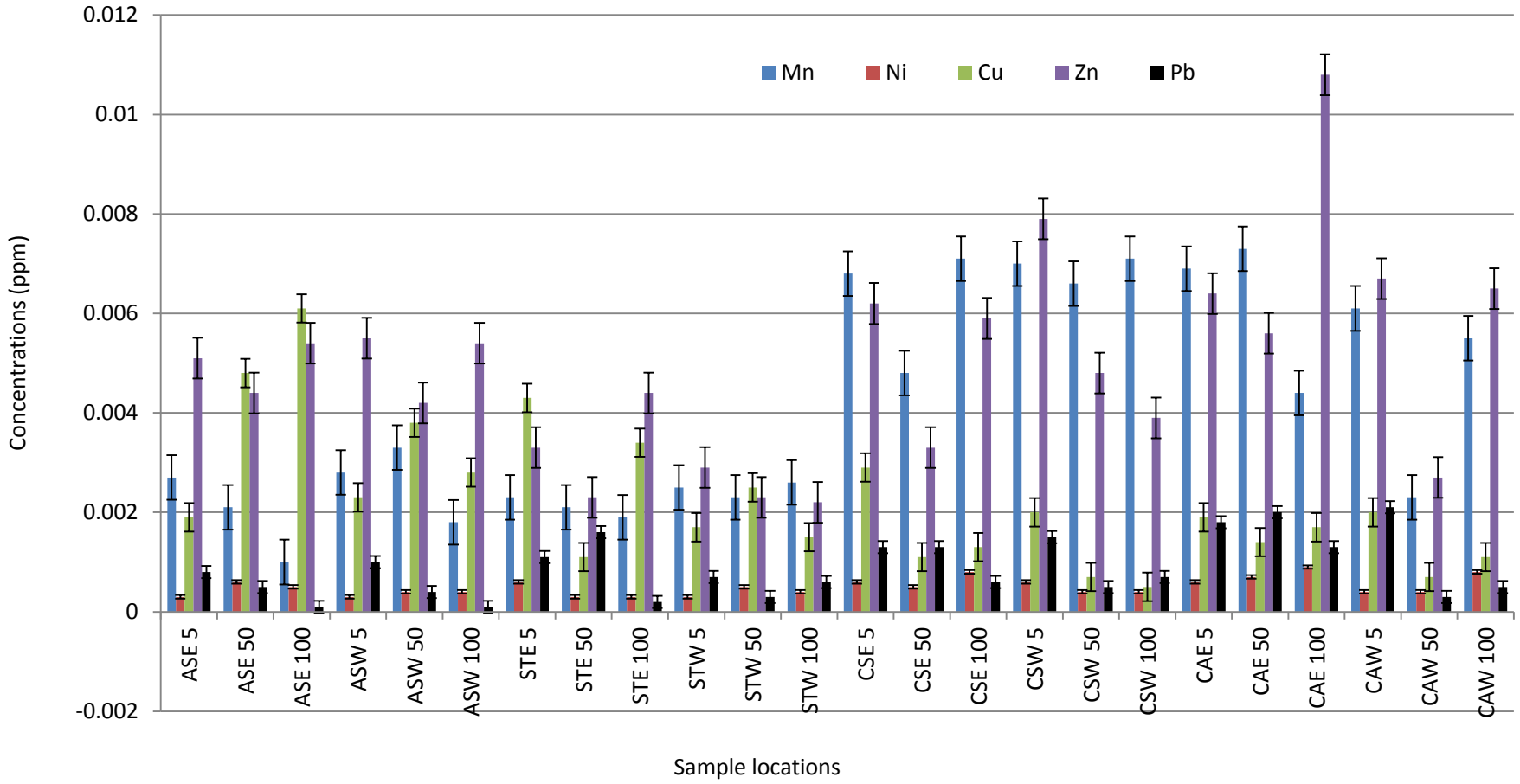


Figure 4.15a: Mid-spring elemental concentrations of ryegrass sample (06.04.10)

Two-Factor analysis of variance show significant difference between the elements (P<0.05), suggesting that the spatial distribution of heavy metals was relatively not uniform while there was no significant difference between the distances (P>0.05) in all four sampling sites, an indication that the spatial variations trend of the elements was not entirely dependent on distance. While **Table 4.16** shows the association between individual elements with others, its relevance is particularly restricted to Pb, Cu, Zn, Ni, Mn, and Ti since they are likely to be of anthropogenic origins.

Table 4.16: Correlation analyses for elemental concentrations of ryegrass sample digest (06.04.10)

	Mg	*Al*	*Ca*	*Ti*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*	*Si*
Mg	1										
Al	0.755143	1									
Ca	0.923861	0.561459	1								
Ti	0.476237	0.773528	0.396523	1							
Mn	0.411388	0.738787	0.228368	0.568725	1						
Fe	0.254491	0.441893	0.123696	0.35294	0.350002	1					
Ni	0.601054	0.504693	0.626973	0.60226	0.502373	0.035862	1				
Cu	-0.10567	0.015899	-0.21583	-0.12907	-0.09229	0.056597	-0.06082	1			
Zn	0.503735	0.536533	0.497157	0.780466	0.299145	0.252493	0.687848	0.073104	1		
Pb	-0.26393	-0.2457	-0.33843	-0.25342	-0.1321	-0.02861	-0.2387	0.683614	-0.09456	1	
Si	-0.30007	-0.19458	-0.38977	-0.29387	-0.2055	-0.24997	-0.25415	0.47227	-0.35501	0.364274	1

4.6.4 Ryegrass in mid-summer season

Results show that Mg, Al, As, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Pb, and Si were among the elements obtained from ryegrass sample during the mid-summer season (15.07.2009) with similar trend of occurrence to the mid-spring analysis. **Figure 4.15b** depicts the trend of elemental concentrations at the four pairs of sampling site. For example, the

maximum value of Si was observed at ASE despite the low daily traffic flow when compared to Craven Arms and Church Stretton sampling sites. The presence of Si may be due to agricultural sources through root uptake or to traffic since they have been associated with break lining components. It may also be due to geogenic or resuspended road dust, as could Fe, Ca, Mg, Al.

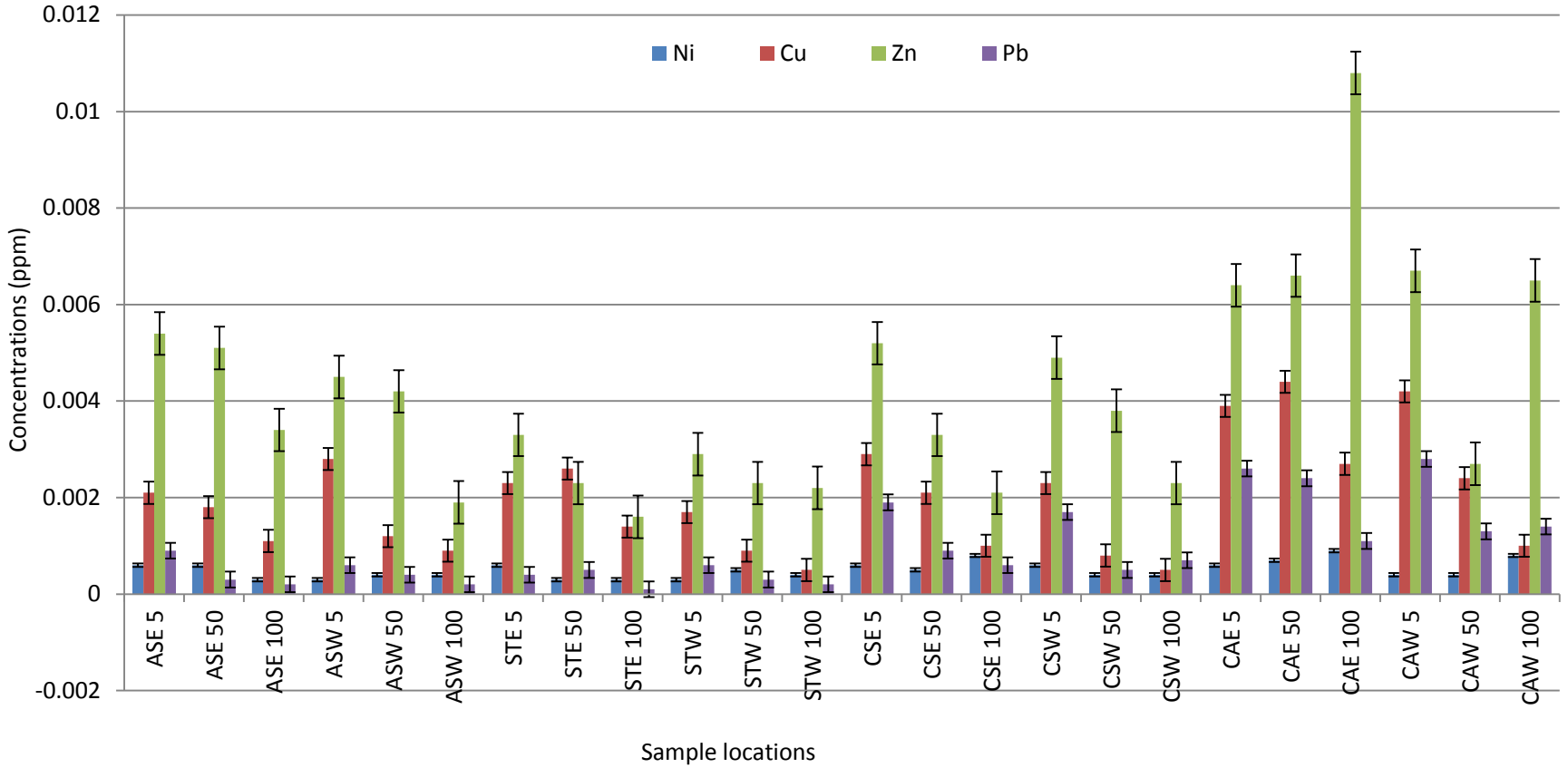


Figure 4.15b: Mid-summer elemental concentrations of ryegrass sample (15.07.09)

To understand the relationship between individual elements with each other, correlation analysis was carried out which shows various degree of association suggesting various sources of the elements (**Table 4.17)**. As stated above, the importance of the association of the elements is particularly limited to Pb, Cu, Zn, Ni, Mn, Cr, and As because they are more likely of man-made origins

Table 4.17: Correlation analyses for elemental concentrations of ryegrass sample digest (15.07.09)

	Mg	*Al*	*Ca*	*Cr*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*	*Si*	*As*
Mg	1											
Al	0.742821	1										
Ca	0.883053	0.606204	1									
Cr	0.599765	0.698097	0.460643	1								
Mn	0.209832	0.160355	0.155307	0.034355	1							
Fe	0.388444	0.817852	0.29888	0.626427	0.039431	1						
Ni	0.152161	0.140242	0.062146	0.289414	0.540218	0.164038	1					
Cu	0.195243	0.497117	0.104542	0.571509	-0.02214	0.769909	0.339611	1				
Zn	0.143825	0.333151	0.18731	0.438952	0.111352	0.557396	0.19671	0.7566	1			
Pb	-0.16388	-0.12278	-0.26478	0.025034	-0.0549	-0.06869	0.256933	0.20672	-0.02233	1		
Si	0.611644	0.917642	0.625703	0.628411	0.088993	0.834051	0.02253	0.468297	0.356137	-0.18865	1	
As	0.086957	0.385089	0.052941	0.446019	-0.0147	0.686866	0.244764	0.892636	0.691411	0.168136	0.375929	1

4.7: ICP results for hazel leaf sample

The multi-elemental analysis of hazel leaf digests shows that elemental concentrations differed with sampling site and location. The mid-spring ICP analysis produced Ca, Cd, Co, Cu, Mg, Ni, Sb, Sr, Ti, Zn, Ba, Mo, Mn, Pb, Cr, and Fe. **Figure 4.16a** shows Cu, Cr, Ni, Ti, Zn and Pb since they are origin is believed to be closely associated to traffic.

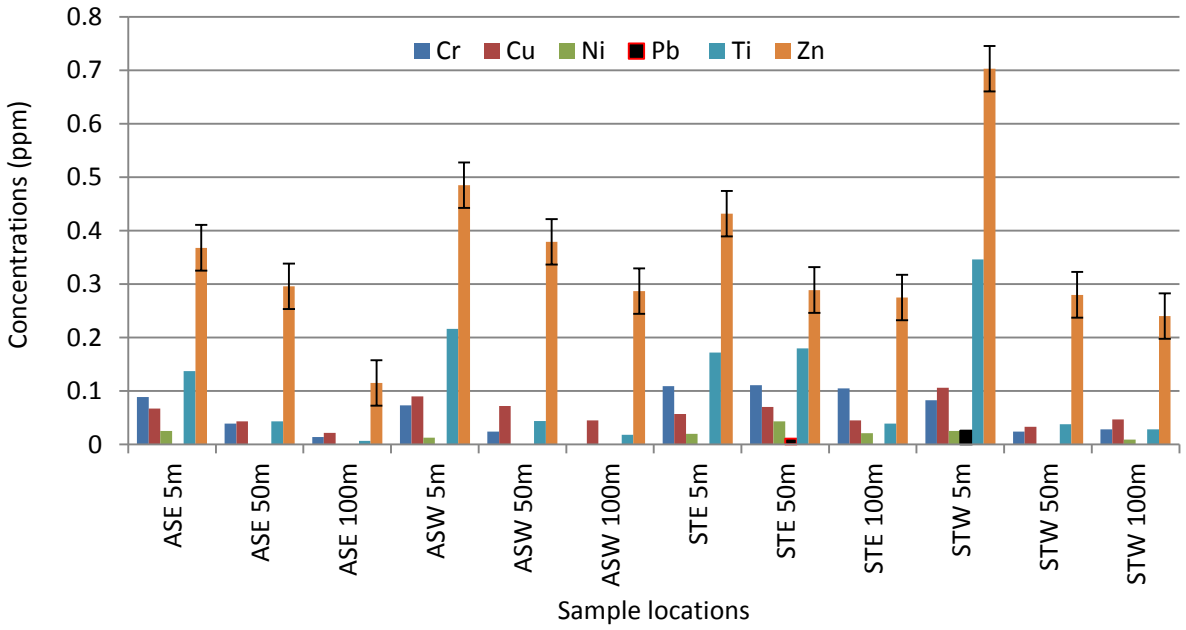


Figure 4.16a: ICP analysis of hazel leaf sample in mid-spring showing (06.04.2010)

When statistical analysis was carried out to test for difference between elemental concentrations, a $P \leq 0.0001$ (5.52×10^{-86}) was obtained, while the difference between distance was not significant ($P > 0.05$) (**Table 4.18**).

Table 4.18: Statistical analyses of hazel leaf sample digest (06.04.2010)

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Distances from the road	143.0923	11	13.0084	1.253991	0.258317	1.861868
Elements	32889.35	12	2740.779	264.2073	5.52E-86	1.826197
Error	1369.314	132	10.37359			
Total	34401.75	155				

Investigating the relationship between the elements require that correlation coefficient analyses be conducted. **Table 4.19** shows the correlation between elements which were observed as strongly positive particularly between Ni and Cr, Ti and Cu, Zn and Cu, Zn and Ti, Ba and Cr, Ba and Ni, Pb and Ti (r^2 between 0.77 and 0.92), suggesting their common source. Some metals exhibited weak correlations, an indication that their common source relationship is low. The correlation between Mn and the other elements was negative, implying that the source of this element may be different from other elements. As above, the relevance of the association is limited to Pb, Cu, Zn, Ni, Mn, Cr, and Ti since they are more likely signatures of anthropogenic origins.

Table 4.19: Correlation between elemental concentrations of hazel leaf sample (06.04.10)

	Ca	*Cr*	*Cu*	*Mg*	*Ni*	*Sr*	*Ti*	*Zn*	*Ba*	*Mo*	*Mn*	*Pb*	*Fe*
Ca	1												
Cr	-0.07079	1											
Cu	-0.12737	0.487706	1										
Mg	0.476122	-0.20866	0.220525	1									
Ni	-0.23722	0.885791	0.52662	-0.00342	1								
Sr	0.636592	0.330005	0.092015	0.647323	0.384103	1							
Ti	-0.27227	0.640941	0.878138	0.036594	0.658333	0.093803	1						
Zn	-0.07018	0.431839	0.899336	0.131826	0.358343	0.004898	0.88071	1					
Ba	0.076883	0.85891	0.695439	0.23352	0.84517	0.554062	0.754967	0.593058	1				
Mo	-0.43652	0.267387	0.196644	-0.53075	0.283041	-0.55951	0.149923	0.096836	-0.02937	1			
Mn	-0.31568	-0.63988	-0.37457	-0.0092	-0.47086	-0.33744	-0.49933	-0.37106	-0.61295	-0.09464	1		
Pb	-0.06339	0.346144	0.66095	0.528016	0.528352	0.381402	0.777202	0.678239	0.616515	-0.1431	-0.27546	1	
Fe	-0.2528	0.480359	0.832915	-0.06107	0.414476	-0.11649	0.927301	0.934831	0.560649	0.136601	-0.3595	0.683604	1

The elemental concentrations of the July 15, 2009 hazel leaf digest ICP analysis is presented in **Figure 4.16b**. It shows that the occurrences of the elements did not follow any regular trend but overall, tend to be higher near the road at each sampling site than farther away from the road.

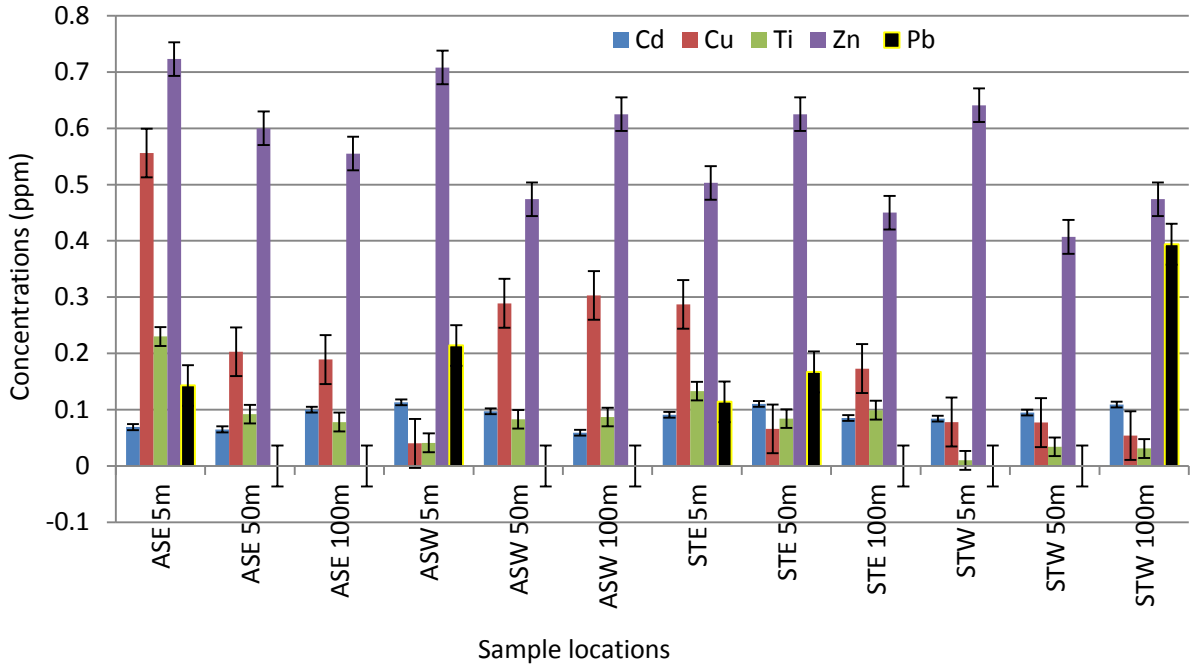


Figure 4.16b: ICP analysis of hazel leaf sample in mid-summer (15.07.2009)

A Two-Factor Anova analysis between distances from the road showed high significant difference ($P \leq 0.0001$). However, the difference between the elements was observed as not significant ($P > 0.05$) (**Table 4.20**).

Table 4.20: Statistical analyses of hazel leaf sample digest (15.07.2009)

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Distances from the road	121178.5	12	10098.21	56.21158	7.14E-46	1.826197
Elements	2314.779	11	210.4344	1.171381	0.312907	1.861868
Error	23713.33	132	179.6464			
Total	147206.6	155				

To determine the relationship between the elements of hazel leaf sample, correlation analysis was carried out. **Table 4.21** shows very strong positive correlation coefficients between Ti and Cu, Sb and Cd, Sr and Cd, Fe and Cu, Mg and Ca, Fe and Ti, and Pb and Cd following that of magnitude. Negative correlation values indicate very weak or negligible relationship between those elements. As above, the relevance of the association is limited to the elements that are more likely of anthropogenic origins such as Pb, Cu, Zn, Mn, and Ti since they are more likely signatures of anthropogenic origins

Table 4.21: Correlation between elemental concentrations of hazel leaf sample (15.07.2009)

	Ca	*Cd*	*Cu*	*Mg*	*Sb*	*Sr*	*Ti*	*Zn*	*Mo*	*Mn*	*Pb*	*Fe*
Ca	1											
Cd	-0.30408	1										
Cu	0.12028	-0.64176	1									
Mg	0.674848	-0.63088	0.359102	1								
Sb	-0.17788	0.888406	-0.55226	-0.45817	1							
Sr	0.868297	-0.00072	-0.20934	0.400694	-0.00838	1						
Ti	-0.15155	-0.46039	0.900622	0.144262	-0.47167	-0.43911	1					
Zn	-0.07331	-0.23228	0.261665	-0.10302	-0.15724	-0.31579	0.301597	1				
Mo	-0.01015	-0.1442	0.347416	-0.03439	0.049575	-0.35692	0.428034	0.459542	1			
Mn	-0.20955	-0.08652	-0.05898	-0.18998	-0.4794	0.032367	0.059916	-0.33988	-0.56645	1		
Pb	-0.66198	0.52819	-0.22173	-0.61805	0.473791	-0.61243	-0.0389	0.138602	0.323793	-0.13014	1	
Fe	0.396979	-0.42689	0.724871	0.409499	-0.38183	0.049612	0.670826	0.515104	0.479168	-0.22166	-0.06898	1

4.8: ICP results for ryegrass sample

The analytical procedure for ryegrass sample digest was the same with the hazel leaf sample. Mid-spring results show the presence of Mg, Al, Ti, Ca, Zn, Si, Fe, Pb, Ni, Cu, Sr, Cd, Sb, Mn, and Mo for all four sampling sites. However, mid-summer results were unreliable due to handling and laboratory errors and are therefore not presented. **Figure**

4.17 illustrates the concentration statuss and trends of selected elements such as Cu, Ni, Pb, Zn, and Ti, whose emissions are known to be traffic-related.

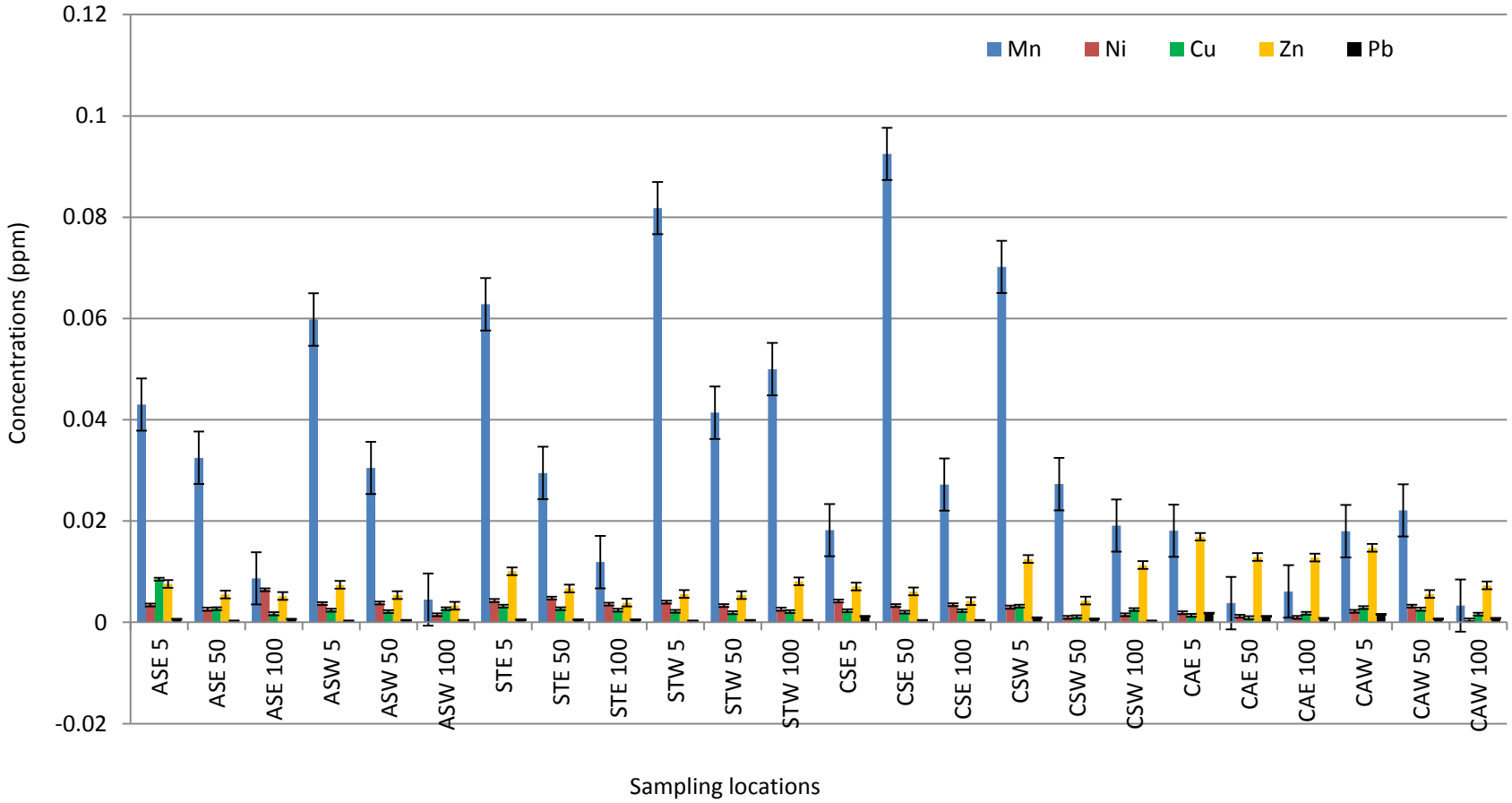


Figure 4.17: ICP analysis showing mean concentration values of ryegrass sample in mid-spring (06.04.2010)

Results were statistically tested to determine the difference between metal concentrations, as well as between distances from the road at all four sampling sites (**Table 4.22**).

Table 4.22: Statistical analyses of ryegrass sample digest (06.04. 2010)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Distances from the road	97.75726	23	4.250316	2.042505	0.004384	1.576367
Elements	1097.284	10	109.7284	52.73038	5.76E-54	1.87203
Error	478.6145	230	2.080933			
Total	1673.655	263				

Significant difference at $p \leq 0.05$ and $p < 0.0001$; No significant difference at $p > 0.05$

Further statistical analysis was carried out to understand the individual relationship of each metal and the other. **Table 4.23** shows the correlation coefficients between elements. However, the degree of relationship between Ca and Mg, Ti and Al, Fe and Al, Fe and Ti, Ni and Mg, Ni and Ca, Zn and Ti, Zn and Fe, Zn and Cu, Pb and Zn, Si and Ca ranged from 0.55 – 0.95, suggesting strong positive correlations, those between Fe and Al, Fe and Ti, and Ti and Al particularly demonstrated very strong relationships. Nevertheless, the relationships were not as strong between the other metals and in some cases negative relationships were observed (e.g. between Ca and Al, Ti and Ca, Fe and Ca, and Zn and Ca), implying either very weak or no relationship between them. Because Pb, Zn, Cu, Ni, Mn, and Ti are more likely of anthropogenic origin than the other elements, the relevance of correlation will be limited to them.

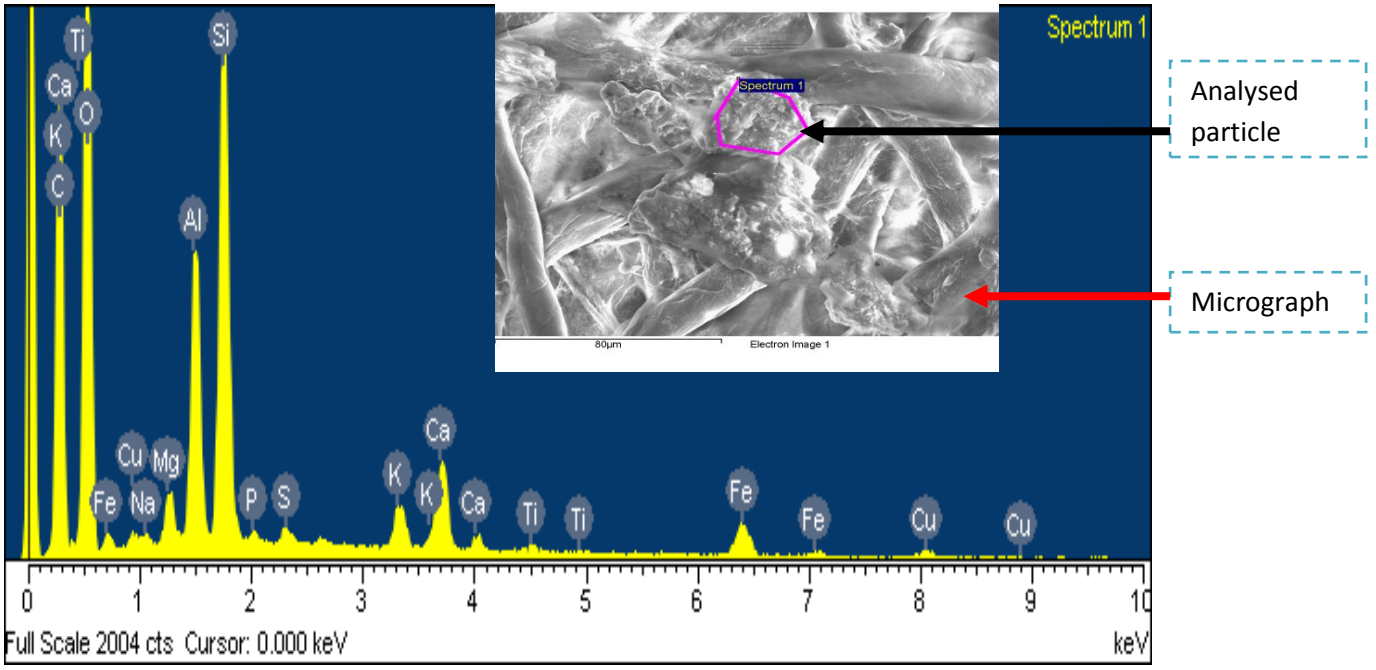
Table 4.23: Correlation between elemental concentrations of ryegrass sample (06.04. 2010)

	Mg	*Al*	*Ca*	*Ti*	*Mn*	*Fe*	*Ni*	*Cu*	*Zn*	*Pb*	*Si*
Mg	1										
Al	0.330988	1									
Ca	0.616067	-0.16468	1								
Ti	0.084866	0.840839	-0.17941	1							
Mn	0.376151	0.482444	0.122997	0.205854	1						
Fe	0.200774	0.902442	-0.14659	0.95176	0.286251	1					
Ni	0.670192	0.270359	0.552671	0.03619	0.576083	0.12859	1				
Cu	0.359425	0.257599	0.26448	0.349886	0.404894	0.400626	0.208459	1			
Zn	0.158434	0.464372	-0.10659	0.572448	0.344741	0.655718	0.102229	0.755188	1		
Pb	0.281038	0.240879	0.190997	0.365398	0.146382	0.465413	0.400815	0.457801	0.613905	1	
Si	0.398371	0.100219	0.722698	0.244359	0.032645	0.272947	0.272038	0.391426	0.139567	0.351832	1

4.9 SEM-EDX analysis of plant samples

The sieved particulate deposits from both hazel leaf and ryegrass samples were characterised the same way by SEM coupled with EDX microanalysis system and observed by backscattered electron images. SEM-EDX images from particles deposited on the surfaces of ryegrass and hazel leaf samples at the roadside of each sampling site are as presented in **Figures 4.18-4.21**. The images shown by the micrographs were of different shapes and sizes. The elements obtained include Ti, Fe, Ca, Zn, Na, S, Si, Mg, Mn, K, P, O, K, Cl, Cu, Mo and Al and were all detected in different percentage weight compositions. Results revealed that Si, Ca, O, Mg, K, Ti, and Al were found in abundance at roadside (5m) samples and showed higher concentrations by some order of magnitudes when compared with SEM-EDX images at 50 and 100 m distances from the road (not shown).

(a)



(b)

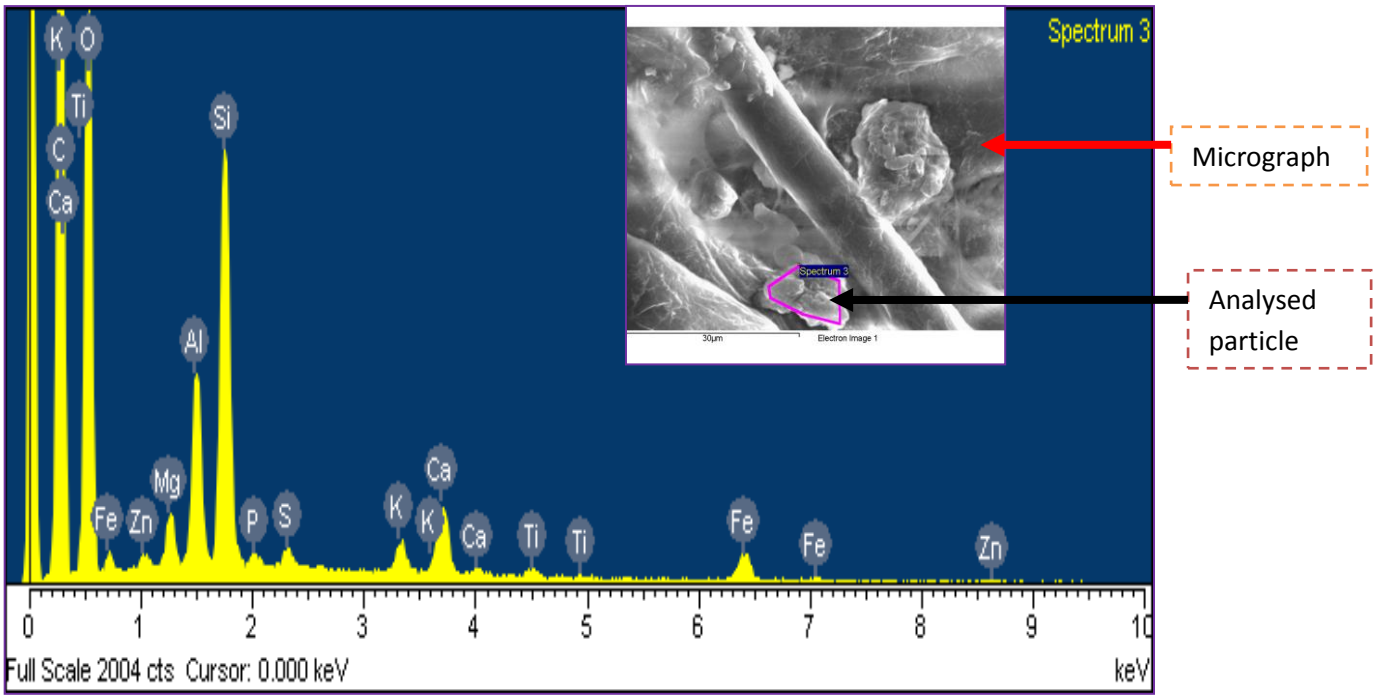
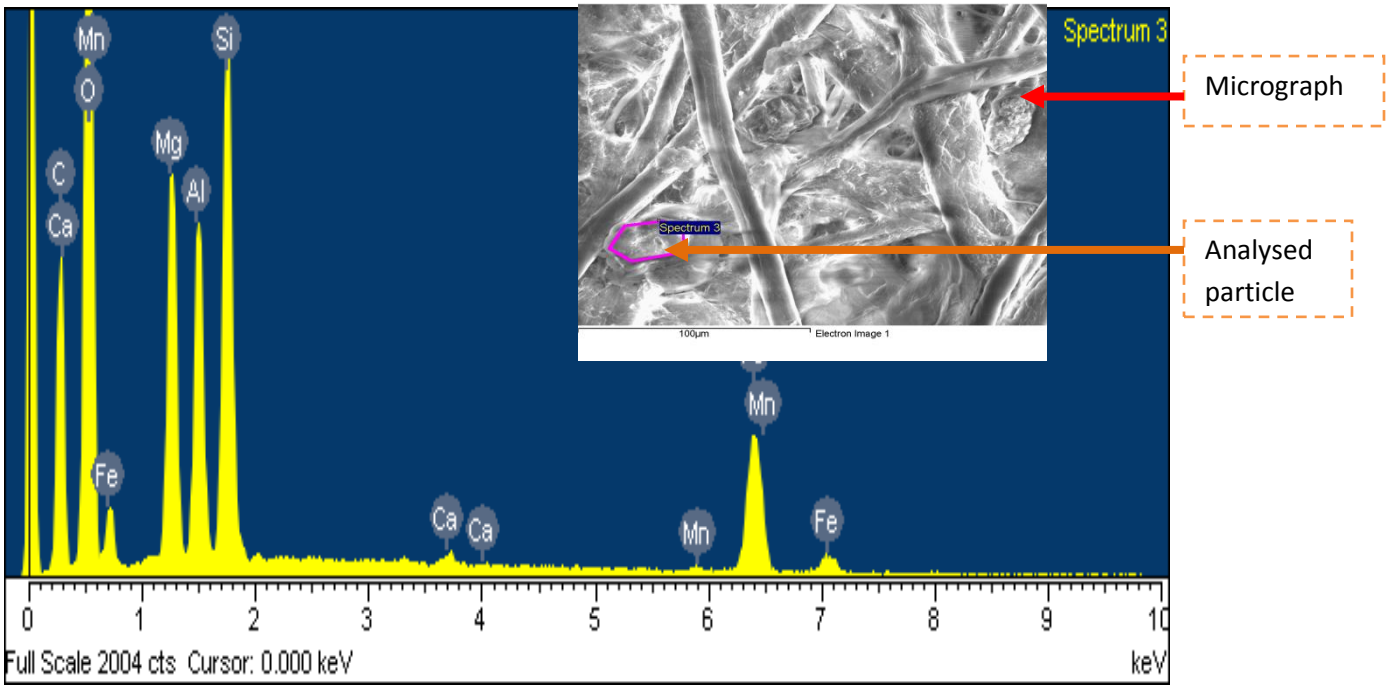


Figure 4.18: X-ray emission spectrum of particles deposited on ryegrass and hazel leaf surfaces analysed by SEM-EDX (inset: Scanning electron micrographs) (a) Ryegrass (b) hazel leaf at All Stretton roadside

(a)



(b)

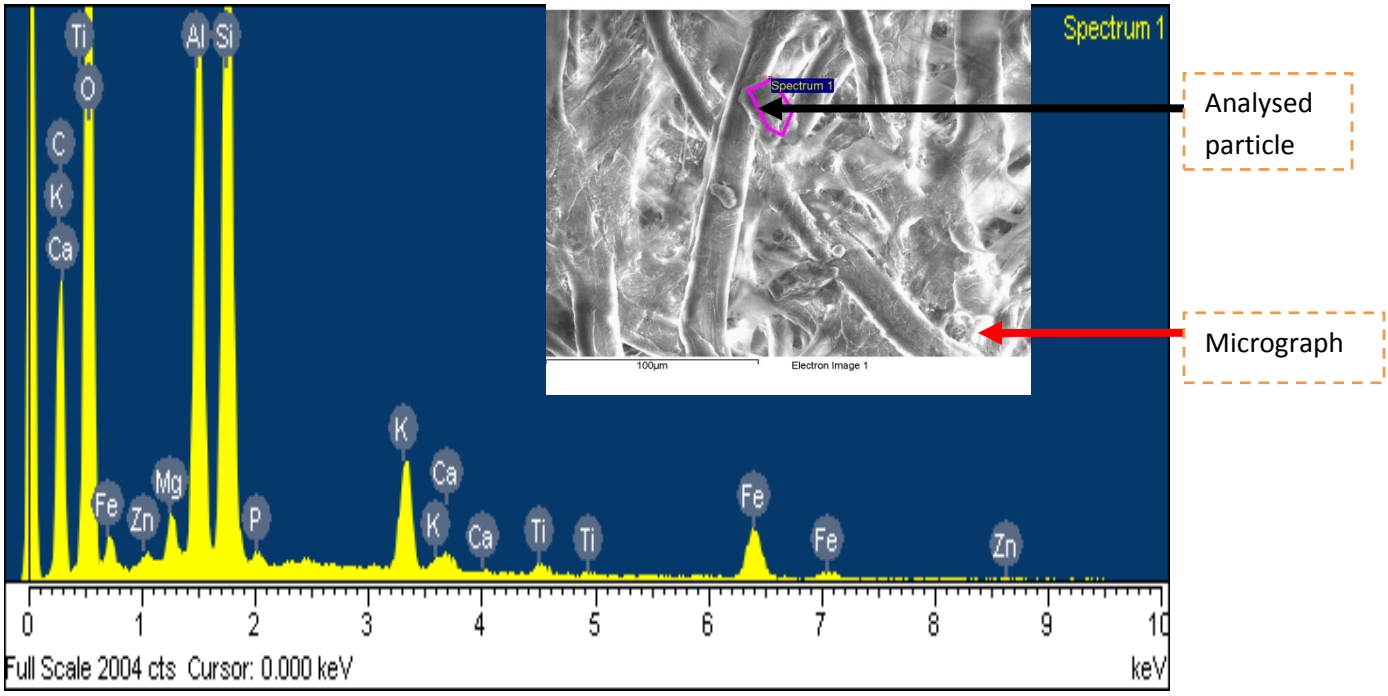
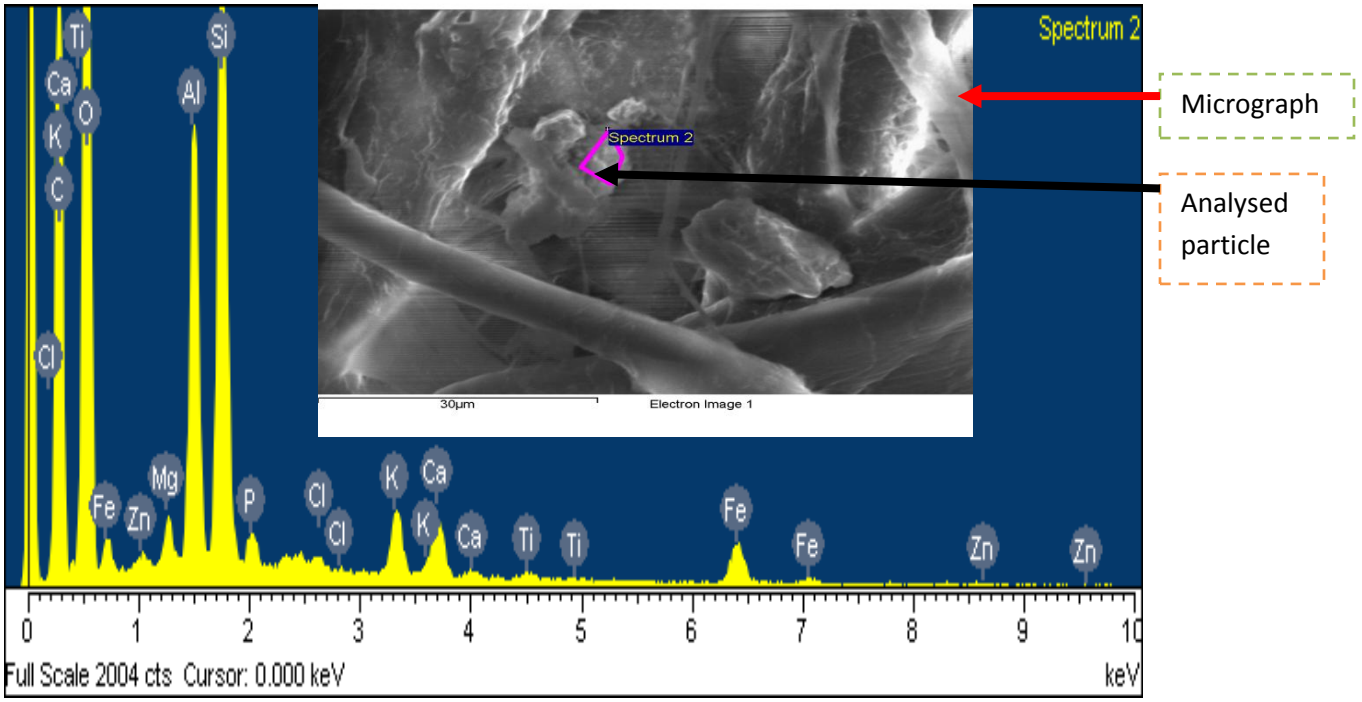


Figure 4.19: X-ray emission spectrum of particles deposited on ryegrass and hazel leaf surfaces analysed by SEM-EDX (inset: Scanning electron micrographs) (a) Ryegrass (b) hazel leaf at Strefford roadside

(a)



(b)

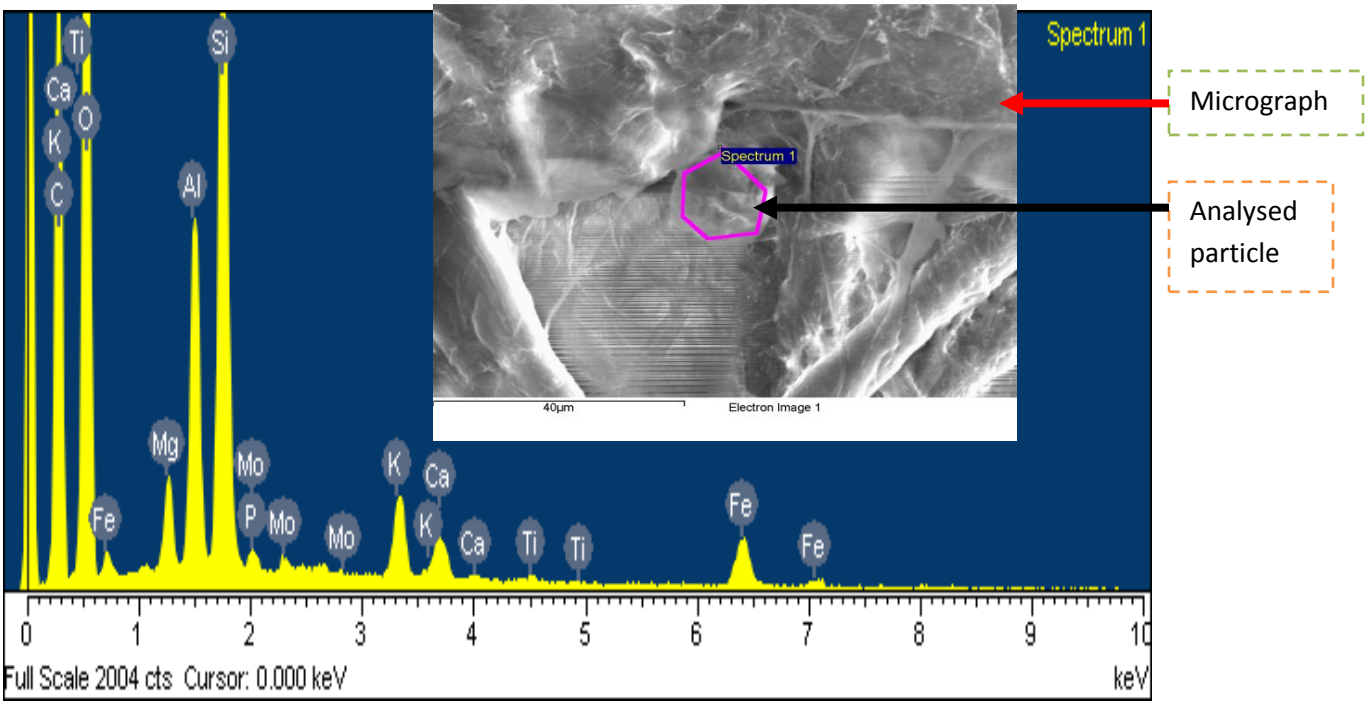
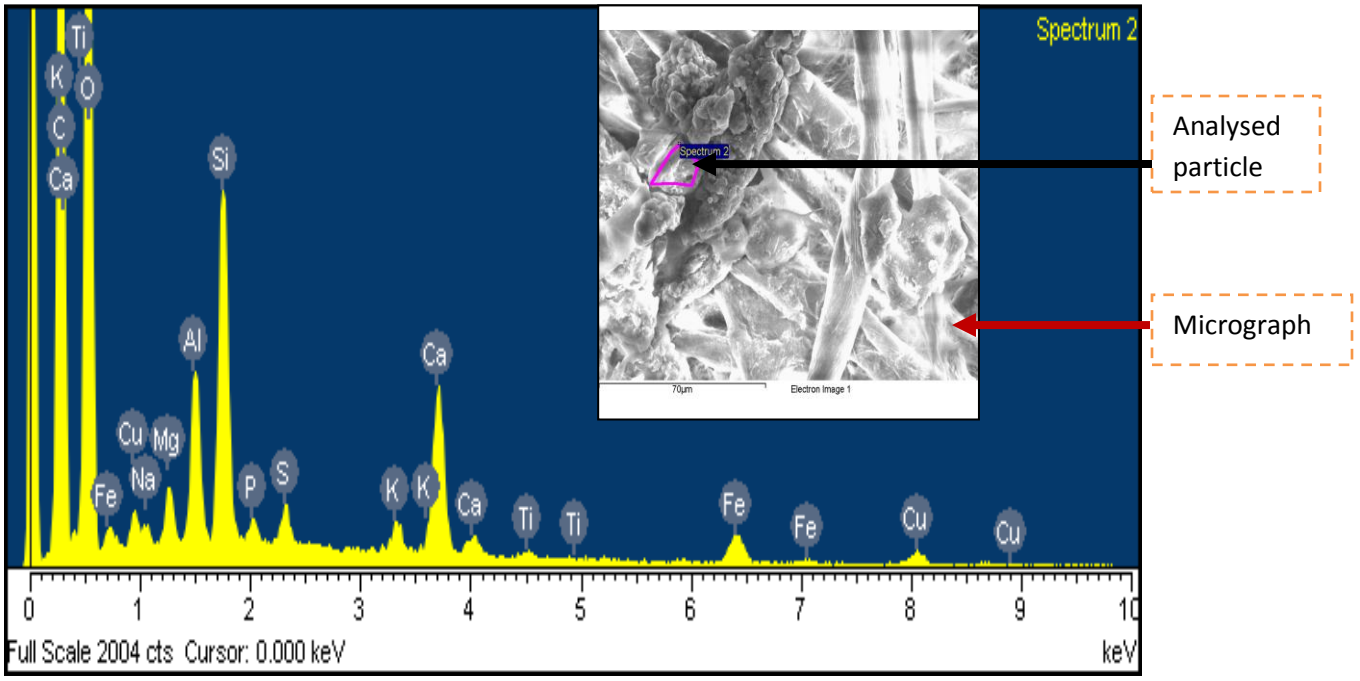


Figure 4.20: X-ray emission spectrum of particles deposited on ryegrass and hazel leaf surfaces analysed by SEM-EDX (inset: Scanning electron micrographs) (a) Ryegrass (b) hazel leaf at Church Stretton roadside

(a)



(b)

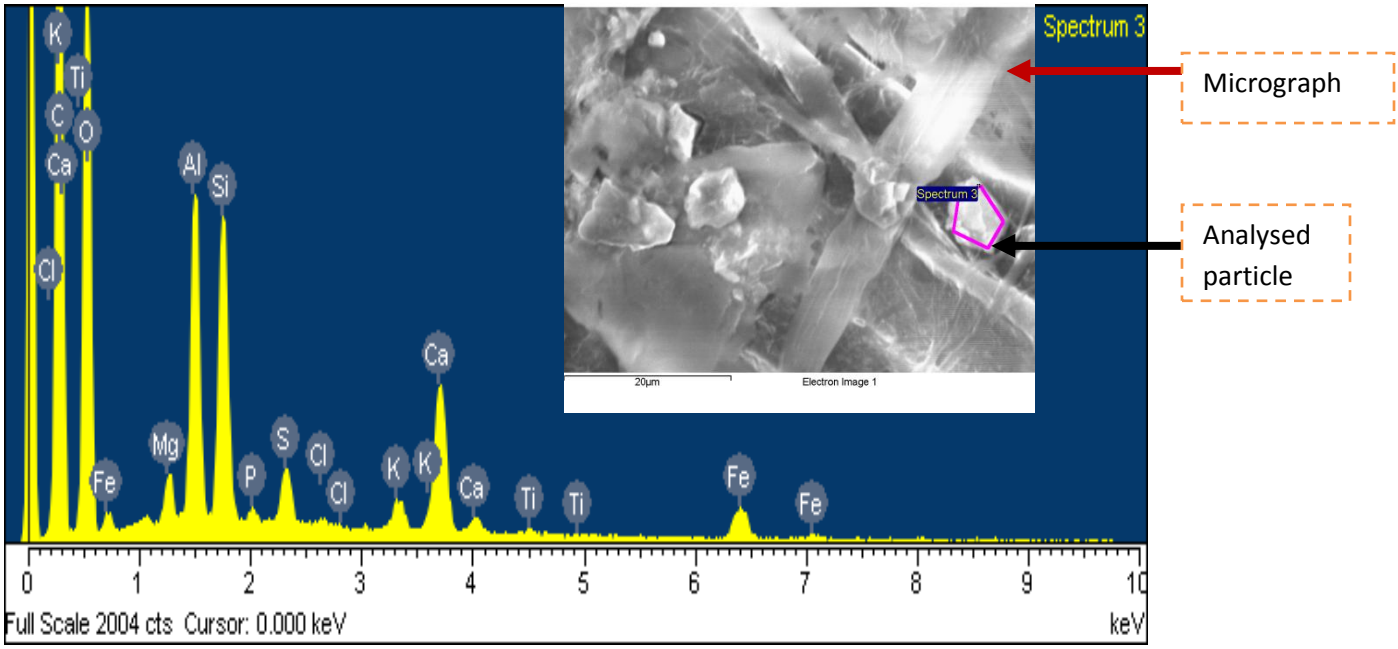


Figure 4.21: X-ray emission spectrum of particles deposited on ryegrass and hazel leaf surfaces analysed by SEM-EDX (insert: Scanning electron micrographs) (a) Ryegrass (b) hazel leaf at Craven Arms roadside

4.10: Inter-technique comparison of ICP and XRF analytical methods

For purpose of data comparability between these techniques, the physico-chemical analysis of ryegrass digest sample was compared by ICP and XRF to determine significant difference and correlation coefficient of pairs of elements. **Table 4.24** shows the relationship between individual elements analysed using ICP and XRF analytical techniques.

Table 4.24: Direct comparison of ICP-MS and XRF-EDX for elemental analysis of ryegrass sample (06.04.2010)

	*Mg**	*Mg***	*Al**	*Al***	*Ca**	*Ca***	*Ti**	*Ti***	*Mn**	*Mn***	*Fe**	*Fe***	*Ni**	*Ni***	*Cu**	*Cu***	*Zn**	*Zn***	*Pb**	*Pb***	*Si**	*Si***
Mg*	1																					
Mg**	-0.32784	1																				
Al*	0.330988	-0.16281	1																			
Al**	0.073311	0.755143	0.063478	1																		
Ca*	0.616067	-0.30388	-0.16468	-0.12273	1																	
Ca**	-0.47375	0.923861	-0.18817	0.561459	-0.44223	1																
Ti*	0.084866	-0.04803	0.840839	0.0786	-0.17941	-0.06104	1															
Ti**	-0.1004	0.476237	0.041713	0.773528	-0.20652	0.396523	0.159159	1														
Mn*	0.376151	-0.36153	0.482444	-0.14888	0.122997	-0.37346	0.205854	-0.24527	1													
Mn**	0.055178	0.411388	-0.02815	0.738787	-0.07706	0.228368	-0.06542	0.568725	-0.17236	1												
Fe*	0.200774	-0.13104	0.902442	0.02718	-0.14659	-0.12224	0.95176	0.091891	0.286251	-0.09447	1											
Fe**	0.063209	0.254491	-0.12931	0.441893	0.35629	0.123696	0.005396	0.35294	-0.2687	0.350002	-0.03294	1										
Ni*	0.670192	-0.20037	0.270359	0.142983	0.552671	-0.27878	0.03619	-0.07997	0.576083	0.009702	0.12859	0.142344	1									
Ni**	-0.49879	0.601054	-0.17937	0.504693	-0.42597	0.626973	-0.07594	0.60226	-0.36578	0.502373	-0.1884	0.035862	-0.36301	1								
Cu*	0.359425	-0.32206	0.257599	-0.19017	0.26448	-0.32807	0.349886	-0.08542	0.404894	-0.18177	0.400626	-0.05888	0.208459	-0.33295	1							
Cu**	0.374754	-0.10567	-0.0398	0.015899	0.470667	-0.21583	-0.05458	-0.12907	0.160353	-0.09229	-0.11907	0.056597	0.354258	-0.06082	0.048959	1						
Zn*	0.158434	-0.3008	0.464372	-0.18805	-0.10659	-0.27156	0.572448	-0.07266	0.344741	-0.20086	0.655718	-0.16872	0.102229	-0.2862	0.755188	-0.21614	1					
Zn**	-0.43383	0.503735	-0.15831	0.536533	-0.39878	0.497157	0.081021	0.780466	-0.36974	0.299145	-0.08027	0.252493	-0.40968	0.687848	-0.21749	0.073104	-0.1723	1				
Pb*	0.281038	-0.25991	0.240879	-0.04064	0.190997	-0.22211	0.365398	-0.09722	0.146382	-0.02916	0.465413	0.116028	0.400815	-0.35872	0.457801	0.039537	0.613905	-0.30404	1			
Pb**	0.389402	-0.25759	-0.16988	-0.2073	0.536717	-0.33476	-0.17991	-0.2664	-0.02394	-0.11875	-0.20507	-0.0372	0.066052	-0.20311	0.067791	0.838921	-0.27054	-0.07119	-0.01782	1		
Si*	0.398371	-0.22381	0.100219	-0.06796	0.722698	-0.27872	0.244359	0.009996	0.032645	-0.15575	0.272947	0.293826	0.272038	-0.39274	0.391426	0.362347	0.139567	-0.12398	0.351832	0.500735	1	
Si**	0.491738	-0.30007	0.079004	-0.19458	0.443826	-0.38977	-0.12816	-0.29387	0.625669	-0.2055	-0.02899	-0.24997	0.487493	-0.25415	0.410915	0.47227	0.238002	-0.35501	0.084155	0.367065	0.138984	1

***: ICP, **: XRF**

4.11: Conclusion

The overall objective of this study was to observe the differences in concentrations of main pollutants depending on the distance from the road. One of the key objectives was to examine the concentration gradients of the measured gaseous pollutants and to compare concentrations of measured gaseous pollutants from both monitoring campaigns.

Throughout the sampling period, sulphur dioxide remained undetected with the short-term hand-held device at all distances along the sampling transects. In contrast, measurements of NO_2 and HC show elevated concentrations at roadside than at the other measurement distances, especially in areas with more traffic frequency. To determine the difference between both pollutants, a paired t-Test analysis between NO_2 and HC pollutants obtained from the first and second measurement campaigns showed significant difference.

Passive diffusion tubes measured SO_2 and NO_2. However, while SO_2 concentrations were beyond NAQS guidance level, NO_2 at 5 m, 50 m and up to 100 m distance measurements exceeded guidance limit.

Another objective was to correlate between traffic frequency (volume) and concentrations of the gaseous pollutants. Regression values differed with sampling site and pollutant. Correlation coefficient between traffic flow and NO_2 was positive (R=0.64, r^2=0.42) at ASE) and at ASW (R=0.29, r^2=0.08) as was HC (R=0.44, r^2=0.20) at ASE and at ASW (R=0.48, r^2=0.23). A positive correlation was also observed between NO_2 and traffic flow (R=0.27, r^2=0.07) at STE and at STW (R=0.51, r^2=0.26). Similarly, HC concentrations

was positively correlated with traffic flow at STE (R=0.44, r^2=0.19), STW (R=0.30, r^2=0.09) as was NO_2 at CSE (R=0.28, r^2=0.08) and CSW (R=0.22, r^2=0.05). Traffic flow correlated positively with HC levels at CSE (R=0.22, r^2=0.05), CSW (R=0.51, r^2=0.26) as was NO_2 at CAE (R=0.25, r^2=0.06), CAW (R=0.35, r^2=0.12) as well as HC at CAE (R=0.28, r^2=0.07) and CAW (R=0.22, r^2=0.04). Further analysis showed the influence of both traffic flow and distance parameters on the spatial distribution of the measured pollutants, being significantly different at P<0.05.

The study considered the influence of wind speed, relative humidity and temperature on the short-term gaseous concentrations of the measured pollutants. It shows that meteorological parameters affected the spatial distributions of the pollutants with relative humidity appearing to exert more influence than the other parameters.

This study also investigated the metal content of hazel leaf and ryegrass samples collected from the sampling sites. Sample preparation depended on the analytical technique. This study used XRF, ICP, and SEM. From the loose ground powder samples of hazel leaf and ryegrass, XRF analysed for Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Si, and Pb. Both the mid-spring and mid-summer results for hazel leaf and ryegrass samples were tested for difference between metal concentrations and produced statistically significant difference (P<0.05)..

Hazel leaf and ryegrass sample digests were analysed by ICP for Mg, Al, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb, Sb, Sr, Mo, Cr, Co, Cd and Si. Concentrations were higher at Craven Arms when compared to the other sampling sites, reflecting the traffic frequency at the sampling sites. In April 6, 2010, hazel leaf sample yielded statistically significant

difference (P<0.05) between elements but no significant difference (P>0.05) was found between distances in addition to strong, weak, and negative correlation coefficients observed between some elements while results from ryegrass sample were significantly different between distances and between elements (P<0.05).

The July 15, 2009 ICP results from hazel leaf sample produced statistically significant difference between distances (P<0.05) from the trunk road while strongly positive, weak, and negative correlation coefficients were all observed between some metals. SEM-EDX was used to characterise Ti, Fe, Ca, Zn, Na, S, Si, Mg, Mn, K, P, O, K, Cl, Cu, Mo and Al. Roadside concentrations were found higher than those from other distances when compared.

The degree of variability of elements between ICP and XRF was analysed using correlation coefficient criterion and it was observed that the degree was element-specific with some elements (e.g. Al**/Al*, Ti**/Ti*, Cu**/Cu*, and Zn**/Zn*) showing a highly reliable relationship between them using both techniques.

Chapter Five

Discussions

5.0 Introduction

The previous chapter provided data generated from both field and experimental techniques that will provide the basis for analyses in this chapter. Analyses will be presented in relation to the outlined aim and objectives and in sections to give clearer understanding of the results.

5.1 Effects of distance on measured gaseous concentrations

Sulphur dioxide was beyond detectable limits using a short-term device. It is not clear why the pollutant was not detected even though transportation has been widely reported as the contributory source (Tan *et al*., 2009). However, it is possible that SO_2 was emitted but at such low concentrations that it was not be detected instantaneously. The reactivity of sulphur compounds when emitted (Lee *et al*., 2008) may have also be a reason why it was not immediately detected, being able to chemically react with water molecules and be converted to sulphuric acid in the atmosphere (Chin and Jacob, 1996) which then precipitates as acid, causing damage to ecosystems and buildings (Lee *et al*., 2008). In addition, the use of lower sulphur fuels and additives in lubricating oils especially in diesel engines (Stanislaus *et al*., 2010) and effective catalytic converters (Amatayakul and Ramnäs, 2001) may have contributed to the non-detectability of SO_2.

The short-term measurements of both NO_2 and HC pollutants were generally higher at roadsides than further distances from the trunk road, an indication of traffic-related source since the roadside location is closest to the trunk road (Brachtl *et al*., 2009 & Chen *et al*., 2009). This finding is consistent with a continuous sampling study by McAdam *et al*. (2011) who examined the distribution of traffic-related air pollution in proximity to a

major road and found elevated levels of gaseous pollutants close to, and decreased with distance from, the major road. Further analyses showed significant difference ($P \leq 0.05$) between distances, indicating that concentrations of both pollutants were affected by distance (Laffray *et al*., 2010), and a negative correlation between measured pollutant levels and distance from the trunk road. This compares with Gilbert *et al*. (2003) who found negative correlation between distance and NO_2 levels and posited that distance from the roadway may be a valid surrogate variable for some traffic-related air pollutants. Regression analysis showed positive r^2 value between pollutant levels and distance, a further indication that pollution levels were strongly associated with distance. This is consistent with Gilbert *et al*. (2003) who found similar association, evidenced by positive r^2 value, between NO_2 concentrations and distance around a busy highway in Canada.

When compared with the four sampling sites, both pollutants were generally higher at roadside distance at Craven Arms sampling site. Craven Arms sampling site is situated near a car park which serves a local shop and accentuates several accelerating and decelerating, stop and go, engine revving, and frequent braking and driving scenarios with the potentials to influence emission rate of pollution (Pandian *et al*., 2009). It is not surprising that elevated levels of the pollutants were detected at this sampling site given that different driving scenarios can emit as much as 10000 ppm hydrocarbon in decelerating and up to 650 ppm of NOx in cruising. Similarly, diesel engine can generate up to 400 ppm of hydrocarbon in idling and about 350 ppm in accelerating modes (Colls, 2002). Staehelin *et al*. (1997) identified gasoline combustion by road traffic as an important source of hydrocarbon suggesting that their occurrence may be due to traffic.

5.2 Influence of traffic volumes on measured gaseous pollutants

The measured pollutants varied between sampling sites in the order of Craven Arms > Church Stretton > Strefford > All Stretton, a trend that reflects the traffic flow differential between the sampling sites and therefore depicts exhaust emission impact, given that changes in traffic frequency parallels changes in emission strengths of the same source (Schitzhofer *et al*., 2008 & Hargreaves *et al*., 2000). Further evidence of vehicular influence was at Church Stretton site. With the presence of traffic light-controlled junction, the maximum concentrations of HC and NO_2 at Church Stretton were next to those at Craven Arms site as was the traffic frequency flow and driving actions. Thus, the observed variation of concentrations of both pollutants along the four sampling sites reflect the traffic flow differentials between sampling sites and the local site conditions (Brachtl *et al*., 2009).

Significant difference ($P \leq 0.05$) between sampling periods signifies positive correlation between traffic flow and NO_2 concentrations since different sampling periods represent different traffic pattern. This relates to the findings of Lau *et al*. (2008) who observed positive correlation between traffic volume and NO_2 concentrations, suggesting that pollutant concentration variations followed traffic flow pattern. Gilbert *et al*. (2007) found similar significant difference between traffic counts and spatial variability of NO_2 and concluded that increased traffic counts can influence pollutant concentrations at locations up to 200 m from the nearest highway. Positive correlation between concentrations of both pollutants and traffic volume (indicated by varying r^2 and *R*-values) is an indication that the spatial distributions of both pollutants were influenced by traffic frequency flow. The degree of influence of traffic frequency on the distributions of

pollutants is represented by the strength of correlation. Thus, higher or lower correlation value is a reflection of the extent of influence of the analysed variable on spatial and temporal variability of both pollutants.

5.3 Measured gaseous concentrations and seasonal variation trends

Because the distribution of pollutants was more variable at the roadside than the other distances from the road, seasonality was limited to the roadside values at all four sampling sites throughout the sampling period. Both pollutants showed a clearly defined trend of variation. Nitrogen dioxide peaked (up to 0.08 ppm) during December-January-February sampling periods, corresponding to winter and consistent to Hargreaves *et al*. (2000) who observed a strong seasonal pattern of variation for NO_2 in mid-winter. Similarly, HC levels (up to 0.93 ppm) were higher during the winter measurement periods (Li *et al*., 2005 & Okuda *et al*., 2002). This may be attributed to temperature inversion (Schnitzhofer *et al*., 2008) commonly associated with winter season since it contributes to the accumulation of pollutants when cold air mass, developed during night-time, effectively traps pollutant in the undermost air layer but breaks up at the development of mixed layer and sunlight (Stull, 2000). During winter, emissions from increased heating, less dilution of pollutants resulting from low mixing height, and slower loss process are possible sources of emissions (Tham *et al*., 2008). That both peak values corresponded to roadside measurement at Craven Arms, a sampling site with higher traffic flow than the other sampling sites, suggests vehicular emission source.

5.4 Influences of meteorological parameters on short-term gaseous pollutants

Because air pollutants differ with traffic and other environmental factors, it was necessary to understand the various influences of some of the parameters such as wind speed, temperature, and relative humidity.

5.4.1 Effects of wind speed on measured pollutants

At low wind speed, it is expected that air mixture and dilution will be low due to weak wind speed strength. This may explain the high level of pollutants close to the emission source and low mean concentrations observed at distances of 50 m and 100 m away at an average wind speed as low as $0.2ms^{-1}$. The interaction between wind speed and NO_2 concentration was significant ($P<0.0001$) at ASE 5, ASW 5, and ASW 50 as was in ASW 5 and ASW 50 for HC. If that was an indication that pollutant levels were influenced by wind speed (Plaisance *et al*., 2004), it is likely that the insignificant correlation observed at further distances was due to low wind speed. In other words, a direct relationship exists between spatial and temporal distribution of pollutants and wind speed, with the former decreasing as the latter decreases. This is in contrast to the inverse association between concentrations and distance, with the former decreasing with increase of the latter (Carslaw *et al*., 2006). However at STW 100, concentrations of pollutants appear to be higher than the preceding distances. While this may require further investigation, it is likely that an elastic-type wind reflection off the windward wall of the canyonic configuration, created by the presence of the South Shropshire Hill, was capable of influencing air pollutant levels at that distance (Chen *et al*., 2009 & Vardoulakis, *et al*., 2002). The positive correlation coefficient was stronger for NO_2 than HC as indicated by

the r^2 and *R*-values. For NO_2, r^2 value was from 0.60 to 0.69 which is higher than 0.35 (maximum) obtained at Daegu in Korea (Jo *et al*., 2005) and for HC, it ranged from 0.39 to 0.66.

5.4.2 Effects of temperature on measured pollutants

The positive correlation coefficient between temperature and concentrations of pollutants gave a significant correlation at $P \leq 0.05$, similar to Plaisance *et al*. (2004) who obtained similar significant relationship between temperature and spatial distribution of NO_2. Results showed positive r^2 values in the range of 0.39 to 0.63 for NO_2 and 0.49-0.55 for HC, an indication that the correlation produced significant effect on the spatial distribution of the measured pollutants along the sampling transect in contrast to the non-significant distances. In the light of positive correlation for NO_2, this finding is consistent with Jo *et al*. (2005) who measured roadside air pollution in Korea and found positive correlation between temperature and NO_2 concentration distributions, but differed in their degree of correlation (0.09-0.48) in contrast to the range obtained from this study.

5.4.3 Effects of relative humidity (RH) on measured pollutants

The influence of relative humidity showed regular trend for both pollutants being significantly associated at $P \leq 0.05$ at some sample locations, indicating that the interaction between RH and concentrations of both pollutants produced significant effects (Plaisance *et al*., 2004) at those distances. Both pollutants also correlated very well as evidenced by their high correlation coefficients. For NO_2: R=0.85, r^2=0.73 and R=0.92, r^2=0.86 for HC at All Stretton sampling site while at Strefford sampling site, R=0.80, r^2=0.64 for NO_2

and for R=0.89 and r^2=0.80 for HC. When compared with other studies, these findings relates with results obtained in Egypt by Elminir (2005) who considered the relationship between air pollutants and relative humidity and found positive association (maximum r^2 = 0.70) and Jo *et al*. (2005) who obtained relatively positive correlation coefficients (maximum r^2 = 0.40) between relative humidity and air pollutants.

5.5 Effects of distance on diffusion tube measurements of NO_2 and SO_2 pollutants

The three-weekly results showed a negative correlation between NO_2 and SO_2 levels with respect to distance with pollutant levels declining with increasing distance from the trunk road. When compared between sampling sites, results showed maximum roadside concentrations for both pollutants at Craven Arms and minimum at All Stretton, reflecting the traffic flow differentials between sampling sites and therefore suggest traffic source since both pollutants followed traffic pattern (Nguyen and Kim, 2006 & Ketzel *et al*., 2003). From the paired T-test analysis, the overall mean concentrations of NO_2 followed the trend of winter (0.208 ppm) > spring (0.168 ppm) > autumn (0.151 ppm) > summer (0.143 ppm). Zou *et al*. (2006) compared NO_2 concentrations near a highway in Shainghai and found similar seasonal trends, so do Ashenden and Edge (1995) who monitored NO_2 pollution in rural environment in Wales using a 2-week exposure diffusion tubes and found higher concentrations of NO_2 in winter (annual average of up to 12 ppb). The trends observed for SO_2 mean concentrations were similar to that for NO_2 except that autumn and summer mean values were the same: winter (0.023 ppm) > spring (0.017 ppm) > autumn/summer (0.013 ppm). This correlates with the findings from Lin *et al*. (2012) who found SO_2 concentrations higher (up to 16.8 ppb)

in winter months than summer in a rural site in China as did Jo *et al.* (2005) in Korea (up to 25 ppb).

The difference between NO_2 in both monitoring campaigns was significant (P = 0.001 and R=0.91) in winter as was in summer (P=0.0003 and R=0.94), spring (P<0.0001 and R=0.84) and during autumn (P = 0.009 and R=0.79). These findings correlate very well, in terms of *p*-values but differ in terms of low *R*-values (maximum of 0.40 in summer), with those of Jo *et al*. (2005). When compared with the NAQS guidance limit, SO_2 mean concentrations at all distances and seasons were below the set limit whereas mean NO_2 concentrations exceeded the guidance limit at roadside (5m) and 50 m distances of all sampling sites and up to 100 m at Church Stretton and Craven Arms sites during the winter measurements (**Figure 4.2**). Exceedance of NO_2 limit was also observed at 5 and 50 m distances from the road during the spring measurements (**Figure 4.3**) and up to 100 m distance from the road at Church Stretton and Craven Arms in summer (**Figure 4.4**) and up to 100 m at Church Stretton during the autumn measurements. This differs with the short-term concentrations of measured pollutants and their difference may due to the advantage of passive being able to absorb the pollutants over a given range of monitoring period.

These findings compare with measurements from Defra (2010) who concluded that there were no areas in UK where hourly mean SO_2 exceeded the limit value of 350 $\mu g/m^3$ from 1990-2010. However, their study shows that the annual mean NO_2 concentrations at urban roadside locations spread throughout most of the UK had annual mean in excess of the limit value of 40 $\mu g/m^3$ in 2010. Similarly, Gadsdon and Power (2009) found

exceedances of NO_2 concentrations at most roadside sites and 20 m away from the roadside across a Special Area for Conservation in southern England using diffusion tube monitoring technique. Pollutants of traffic origin are likely to make increasing contribution not just to the exceedance of critical levels, but also of critical nitrogen loads to adjacent habitats especially with the predicted increases in car ownership and usage in the future (DETR, 2005). Hourly exceedences are driven by meteorological conditions and show considerable year-to-year variability. These exceedances are very likely to have long term ecological implications for adjacent habitats of plant species associated with higher levels of nitrogen availability (Truscott *et al*., 2005), and for people living in the immediate vicinity of, and up to 100 m from, the trunk road.

5.6 Elemental analysis of hazel leaf and ryegrass digest samples by XRF

5.6.1 Hazel leaf sample

Results showed the presence of different heavy metals at various concentrations among the heavy metals. There was a common trend observed for Cr, Cu, Ti, and Zn, where maximum concentrations declined with increasing distance from the trunk road, indicating a road source. However no regular trend was observed for Ca, Mg, Sr, and Mn and this contrasting result indicates that those elements were likely not of anthropogenic origin because the presence of crustal elements (Al, Si, Mg, Ti, Fe, Mn, Cr, Ca, and Sr) are traced to re-suspended material origin. Interestingly, it was observed that maximum occurrence of Cr, Cu, Mg, Ni, Sr, Ti, Ba, Mo, and Pb was at 50 m location point, coinciding with a Farm House road junction at Strefford East transect which serves as entry and exiting point for tractors and personal private cars to and from the farm house. This trend therefore suggests anthropogenic source.

Amongst the heavy metals, Pb is of significant importance due to their constant increase in the environment and the potential hazard to health it possess. Lead concentrations were low at all sampled sites despite the traffic flow differentials, thus conflicting with the expectation of elevated Pb concentrations near roadways since Pb roadside deposition is generally associated with traffic density and distance from road (Naveed *et al*., 2010 & Wåhlin *et al*., 2006). The observed low levels of Pb may be due to the phasing-out of unleaded fuel (Rode *et al*., 2010). It may also be because root uptake of Pb from soil into plant leaves is unlikely since it is a heavy metal with low plant mobility (Günthardt-Goerg & Vollenweider, 2007) or because Pb is not able to penetrate the cuticles of higher plants (Radojević & Bashkin, 2006). These scenarios therefore suggest that the origin of Pb was from atmospheric depositions of particulates on plant surfaces. Lam *et al*. (1999) measured the Pb content of grass at various distances from the road and found a well-defined linear pattern of concentrations falling from maximum at close proximity to the roadside to an overall minimum level at distances further away from the road. Lead components, tetraethyl lead (found in leaded gasoline) and tetramethyl lead, are used as anti-knock additives in petrol. Even though leaded petrol has been phased out in the UK, combustion of unleaded gasoline is still a source of Pb emissions (Pacyna *et al*., 2007) especially given that the fraction of Pb found in petrol has been confirmed as a natural fuel impurity that will not be removed during the refining process (Kummer *et al*., 2009).

A comparative analysis of Pb in hazel leaf sample from both sampling season shows that the metal was correlated positively with the analysed elements but showed the strongest correlation with Mn (0.7789) in mid-spring slightly higher than in mid-summer (0.7786). Lead/Ni also demonstrated a positive correlation that may be due to traffic source

because Pb and Ni have mainly been associated to fossil fuel emissions (Dedeles *et al*., 2000) or as constituents of crude oil (Pacyna *et al*., 2007). However, their association was weak in mid-spring (0.34) and in mid-summer (0.33), suggesting a seasonal variation. These findings somewhat differ with those of Naveed *et al*. (2010) who found higher Pb levels in summer than winter in a rural environment using other plant leave species and Lam *et al*. (1999) who found marked seasonal variation in Pb using another plant leave specie in Birmingham, England with maximum level in autumn. Low Pb level in leave (different from those used here) has also been reported in a rural site in Iran (Poukhabbaz, *et al*., 2010). From the correlation analysis, individual metals showed strong positive association with one another in the following ranking order Fe/Al (0.98), Fe/Ti (0.98), Fe/Mg (0.92), Ti/Al (0.96), and Al/Mg (0.96). Results show elevated levels of Fe, Al, Mg, and Ca at roadside measurements therefore they are likely to represent their particular origin within the overall traffic source. Fuels, lubricating oils or other additives are sources of Al (Miller *et al*., 2007) while their association with Fe is a marker of soil origin (Fang *et al*., 2003). Chromium, Cu, and Fe have been linked to brake wear (Harrison *et al*., 2003) and in addition to Zn, Ni, and Pb have been associated with particulate pollution from roads (Peachey *et al*., 2009) suggesting that their strong correlation with other elements depict traffic origin (Riga-Karandinos and Saitanis, 2004). However, negative correlation coefficient was observed between Arsenic and other metals except for very weak positive association with Ti (0.006) and Mn (0.09). Titanium is a possible tyre wear emission source (Sanders *et al*., 2003) and Mn has been associated to heavy fuel combustion source (Dore *et al*., 2007 & Fernando *et al*., 2006). Although the emissions of Cu, Ni and Zn from road traffic have been confirmed (Winther

and Slentø, 2010) these elements are essential elements and therefore their presence (concentrations) may also accentuate the physiological processes.

Significant difference was observed between the elements in hazel leaf sample at the three site pairs (P = 0.007), suggesting that the elements in hazel leaf were widely distributed in all three sampled sites.

5.6.2 Ryegrass sample

From mid-spring ryegrass sample, Ni, Mn and Zn correlated positively with all analysed elements, while the association between Pb and other elements yielded positive correlation only with Cu while Cu produced positive association only with Al and Fe. During mid-summer sampling period Mn, Ni, and Zn correlated positively with all analysed elements but the association of Pb only yielded positive with Cr, Ni, and Cu. Copper correlated positively with all analysed metals except Mn. Positive correlations denote possible common source of origin between the correlated pair of individual elements. Nickel and Mn mainly originated from combustion of heavy liquid fuels while Zn is mainly from road transport resulting from tyre wear (Dore *et al*., 2007). Lead/Cu, Cr, and Ni were positive, an indication of road traffic origin while Cu/Al and Fe may indicate a road transport source (Dore *et al*., 2007) and therefore provide evidence of vehicular influence on elemental deposition on leaf and grass surfaces.

From ryegrass sample, significant difference ($P \leq 0.05$) between elements was found at ASE and between distances (P = 0.07) from the trunk road. Similarly, the difference between sample distances from the trunk road was significantly different at P = 0.03, an

indication that distance had a significant impact on ryegrass elemental levels and $P = 0.06$ found between the elements at ASW shows elemental variation. At both pair of Strefford sampling site, significant differences were observed between the elements at $P = 0.002$ and $P = 0.01$ respectively at STE and STW while differences were not significant between distances ($P>0.05$) from the trunk road.

The differences between elemental concentrations and distances from the road were also tested in CSE. The former was observed as significantly different ($P<0.0001$) as opposed to the latter with no significant difference ($P>0.05$). Church Stretton West site followed similar trends.

At Craven Arms East sampling site, both elements and distances were significantly different ($P<0.05$), an indication that the distribution of the elements on ryegrass was influenced by distance. Therefore, it is expected that plants near roadways will comparatively be prone to heavy metal pollution due to vehicular emissions (Li *et al*., 2007). At Craven Arms West, the difference between elements was statistically significant ($P = 0.007$), but was not significant between distances ($P>0.05$).

5.7 Elemental analysis of hazel leaf and ryegrass digest samples by ICP

5.7.1 Hazel leaf sample

The mid-spring hazel leaf sample showed that the elements did not demonstrate any particular pattern in their occurrence throughout the measuring campaign. Elevated roadside Zn level (0.368 ppm) at 5 m was in magnitudes of 1.2 times more than at 50 m and 3.4 times higher than at 100 m at All Stretton East and about 1.3 and 1.7 times more than at 50 and 100 m respectively away from the trunk road at All Stretton West site. At

Strefford East, elevated roadside Zn concentrations (0.432 ppm) was 1.5 times higher than concentrations at 50 m and 1.6 times greater than at 100 m while the Strefford West sampling site produced elevated road concentrations of Zn (0.703 ppm) equivalent to 2.5 times that at 50 m and 2.9 times higher than Zn levels at 100 m from the trunk road. Concentrations of Cr, Cu, Ni, Pb, and Ti also exhibited inverse relationship with distance, decreasing in levels with increasing distance from the trunk road. However, the trends of these heavy metals occurrence appeared to be altered at Strefford East sampling site where concentrations at 50 m correspondingly exceeded the 5 m heavy metal levels. Of particular interest is Pb which was only present at this location along this sampling transect. This sampling site is situated at the entrance of a farm house and provides access to vehicles and tractors to and from the farm house. These trends are clear evidences that suggest that levels of some heavy metals could be linked to, and act as indicators of traffic pollution.

To compare the trends and relationships between heavy metals, statistical analyses were calculated. Chromium exhibited a strong positive correlation with Ni (0.88) and weak association with Mo (0.26). While such correlations may be partly ascribed to their presence in steel alloys (Johansson *et al.*, 2009), there are no steel industries within the sampling sites and therefore the presence of these metals may signify anthropogenic sources including fuel combustion and vehicle brake debris (Pacyna *et al*., 2007 & Birmili *et al*., 2006). There was no correlation between Pb and Mo, Ca, and Mn, reflecting the possibility of different emission source from Pb. In contrast, the mid-summer hazel sample yielded a positive correlation between Pb and Mo (0.32), suggesting the likelihood of seasonal impact. The presence of Mo may be due to pollution

from automotive source since this metal has been associated to emission from catalytic converter erosion and deterioration and Mo showing a positive correlation with Ni (0.28) is an evidence that emission of these metals may be due to traffic (da Silva *et al*., 2008). Previous biomonitoring studies (e.g., Lehndorff *et al*., 2010) showed similar correlation and ascribed to vehicular emission. The correlation between Pb and Ti (0.77) from the mid-spring hazel sample contrast that of the mid-summer (-0.03), suggesting that seasonal change may have influenced the correlational association between both metals. However the correlation of Pb and Mg (0.52) may be attributed to road and pavement erosion source (Arditsoglou and Samara, 2005) while the association between Pb and Ba (0.61) and Zn (0.67) can be ascribed to vehicular emission having been proposed as a reliable indicator of unleaded fuel and diesel oil powered motor vehicles (Monaci *et al*., 2000). Similarly, Lead/Cu (0.66), Pb/Mg (0.52) and Ni (0.52) may be associated to vehicular emission source since Pb has been a useful marker of exhaust emissions (Thorpe & Harrison, 2008). Iron and Ti exhibited a positive correlation (0.92) as Sr and Ca (0.63) and are linked to the influence of re-suspended materials ((Arditsoglou and Samara, 2005).

Statistical analysis of mid-spring hazel sample showed no significant difference ($P = 0.2$) between distances from the road, suggesting that the spatial distribution of metals in hazel leaf sample was not totally influenced by distance from the road during this sampling season. However, significant difference was observed between elements ($P = 5.52 \times 10^{-86}$), suggesting variability of elemental distribution in hazel leaf sample. There was significant difference between distances in mid-summer hazel leaf sample ($P = 7.14 \times 10^{-46}$), indicating that elemental distribution in hazel leaf sample was influenced by distance

from the road. However, no significant difference was found between elements (P = 0.3), implying that even though distance influenced particulate deposition on leaf, their level in leaf was relatively uniform.

5.7.2 Ryegrass sample

The mid-spring correlation coefficient analysis revealed positive association between Pb and the analysed elements. While the strongest was with Zn (0.61), the weakest was with Mn (0.14). Lead/Zn was higher in leaf digest sample (0.67) than in ryegrass. Although Zn did not show consistent distance-decay behaviour, many roadside measurements were observed at elevated levels than at other distances along the same transect, suggesting a road source, considering that Zn is a known useful marker of traffic flow (Pearson *et al*., 2000) and an indicator of oil-burning and transportation (Adamo *et al*., 2008 & Äyräs and Kashulina, 2000). The occurrence of Zn can likely be traced to the addition of Zinc oxide to tyres as an activator for the vulcanization process and sometimes used as reinforcement to tyre structure (Dore *et al*., 2007 & Kennedy and Gadd, 2003).

Manganese correlated positively with all analysed elements in ryegrass in contrast to the negative correlation it exhibited in hazel leaf sample during the same sampling period. The positive association of individual elements with Mn portrays a common source which is presumed to be anthropogenic since the presence of Mn has often been used as indicators of fossil fuel combustion, incineration (Gao *et al*., 2002) and mainly from combustion of heavy liquid fuels (Dore *et al*., 2007).

The presence of Fe and Al in both mid-summer and mid-spring hazel leaf sample did not follow a general defined trend. While the former (Fe = 0.52 ppm) and the latter (Al = 0.92 ppm) tend to be dominant at All Stretton West, Fe (0.17 ppm) and Al (0.4 ppm) were dominant at Church Stretton West. Their presence suggests either local emission from road source or indicators of lithogenic source (Ebert *et al*., 2000). This relates to other biomonitoring studies, e.g., Klumpp *et al*. (2009) who used ryegrass to monitor airborne trace element pollution after 4 weeks of exposure and found that the trend of elemental occurrence did not follow any regular trend. The association of Fe with Mn, Zn, and Cu is a known good indicator of anthropogenic emissions such as fossil fuel combustion (Gao *et al*., 2002) while Fe/Ti (0.95) was higher in ryegrass in comparison to hazel leaf sample (0.92) and their very strong correlations depict a common source for both metals. The correlations of Fe/Al (0.90) may be due to fly ash pollution usually generated during the combustion of coal (Ahmaruzzaman, 2010).

While root uptake of some elements from the soil proves to be a potential source, the valley in the study areas are filled with a somewhat thick veneer of glacial and post-glacial outwash products, predominantly comprising sands, gravels silts and clays. The true thickness of these Quaternary deposits is difficult to estimate, but the depth to bedrock may be up to 50 m in the valley itself (Allbutt *et al*., 2003). Most of the superficial sediments are derived locally from the Precambrian Longmyndian Supergoup Series, which are predominantly sedimentary in origin with some volcanic tuffs, and these can be located in the hills to the west of the valley. The Uriconian Volcanic Series are located in the hills immediately to the east of the valley, e.g. around Caer Caradoc, and are comprised of lavas an ashes of various chemical composition (Toghill, 2000). As

the Precambrian rocks in the study area are not associated with any form of extensive mineralisation (Allbutt *et al*., 2003), it follows that the finer argillaceous sediments in the valley do not contain elevated concentrations of heavy metals. Elemental concentrations of Zn, Pb, Cu, Fe and Ni are thus expected to be within the normal range of background levels for the Welsh Borderlands. The sandier soils in the areas around the sampling locations (cf. **Figure 3.1**) are dominated by quartz grains and so would be expected to have low elemental concentrations in the absence of any volcanic mineralisation in the catchment. Consequently, anomalous elemental concentrations in particulate deposits on leaf and grass surfaces collected in this research are probably not derived from geological sources.

Statistical analysis show that difference between elements was very significant (P = 5.76 x 10-54), suggesting variation of elemental distribution in both plant samples. Both analyses therefore support a distance-decay trend of elemental distribution.

5.8 Inter-technique comparison of ICP and XRF methods of elemental analysis

The inter-technique comparison of the elemental concentrations from ICP and XRF was analysed. The association between the pairs of each individual element produced very poor correlation for Al (r^2 = 0.06), Ti (r^2 = 0.15), Cu (r^2 = 0.04) and Zn (r^2 = 0.13) and correlation was lost for other analysed elements. This may be due to limited particle mass present in the vegetation samples collected leading to very low concentrations detection of the elements by both analytical approaches. The low detection may be ascribed to the washing process during sample preparations. It is also likely that procedural contamination such as handling, transportation, and laboratory processes may have

contributed to the poor correlation of individual elements. This was justified by Niu *et al*. (2010) who concluded that field processes contributed 76% of Pb contamination while laboratory procedures such as weighing, digestion, grinding, and determination processes accounted for up to 97% of main pollutants for Zn and Cu. There is also the chance of unknown sources of metal contamination that accumulates during sample handling process capable of exceeding the contributions of the particles themselves if no adequate precautionary measures are observed (Rasmussen *et al*., 2006a).

However, individual statistical analysis of the elements yielded significant difference for Mg ($P = 4.2 \times 10^{-8}$), Al ($P = 0.0003$), Ca ($P = 4.42 \times 10^{-6}$), Ti ($P = 0.04$), Mn ($P = 7.9 \times 10^{-5}$), Ni ($P = 3.41 \times 10^{-8}$), Zn ($P = 0.01$), Pb ($P = 0.07$), and Si ($P = 0.009$). This is an indicating that there is no bias in using both approaches for the detection of the elements. However, no significant difference was obtained for Fe ($P = 0.8$) and Cu ($P = 0.8$), suggesting bias in the detection of both elements assuming contamination is highly minimised.

5.9 Elemental analysis of hazel leaf and ryegrass digest samples by SEM-EDX

The SEM photomicrographs revealed the chemical composition of the particles deposited on hazel leaf and ryegrass samples. Elemental detection varied with sampling sites and samples. At All Stretton sampling site, Si and Al were more in abundance in roadside ryegrass sample than was in hazel leaf and Cu and Na were only detected in ryegrass sample as was Zn in hazel leaf. Similarly at Strefford sampling site, Mn, Si, Mg, Ca, C, and Al were dominant at roadside ryegrass sample as were Ti, Al, Si, C, K and Ca in hazel leaf than the other distances. At Church Stretton sampling site, Zn and Cl were only

found in ryegrass sample as was Mo in hazel while at Craven Arms the presence of Na and Cu at Craven Arms was only in ryegrass and Cl found only in hazel leaf sample.

It is conceivable therefore to argue that the elevated presence of these elements near road has to do with source(s) emanating from the road. This is because road dust, a mixture of natural and anthropogenic components, is characterized by high concentrations of mineral components such as Ca, Al, Fe, Mg and Si (Karanasiou *et al*., 2011) and in addition to K, exist predominantly in soil and common in re-suspended dust (Han *et al*., 2011 & Kim *et al*., 2006). There is therefore a possibility that the presence of these elements is very much likely a source contribution of re-suspension of soil particles especially considering that traffic may result in increased generation of tire wear, brake wear, and road surface wear dust which will contribute to the overall re-suspended soil particle dust. The presence of Si provides a typical evidence of the soil-related source of the elements being the most abundant elements in soil and thus may depict re-suspended road dust source (Han *et al*., 2011).

Iron particle profile could be partly from soil but because of the lack of elemental analyses of local soil to confirm otherwise, Fe might be partly from rust from any iron object which may not be limited to vehicles. Vehicle-related source contribution of the elements is also possible considering that Al have been previously linked to fuel, lubricating oils, or their additives (Miller *et al*., 2007) and Ca, K, and Mg have been found in deciduous leave samples and reflect the contribution from oil combustion processes (Tomasévić *et al.*, 2005). Previous studies have provided evidence to show that despite the abundance of Ca, Mg, Al, Si, Fe, and K in soil, they have been mainly derived

from natural sources and Fe and K have been emitted from various anthropogenic sources including vehicle exhausts, industrial processes, coal combustion, and oil burning (Fang *et al*., 2010 & Wu *et al*., 2007). In the absence of industries and coal combustion within the sample locations, the possibility of both sources is very unlikely. However, Na, Ca, Mg, and K have also been strongly linked to sea salt (Kim *et al*., 2006).

The occurrence of Cl was found to correspond to sampling sites with higher traffic volume and suggests that they are predominantly of anthropogenic source. There is the likely possibility that the presence of Cl is related to the salt used during winter to prevent ice formation on the road level (Wang *et al*., 2001) or may have originated from wear dust particles (Tomašević *et al*., 2005). The presence of Zn and Cu is presumably indicate traffic-related source since Zn represents tire wear emission on one hand and on the other hand Cu represents brake wear emission. Their occurrence therefore provide an indication of a relationship between traffic and road dust source (Gietl *et al*., 2010; Amato *et al*., 2009a & Thorpe and Harrison, 2008) while previous studies (e.g. Amato *et al*., 2009) have revealed a strong link between Mo and wear of brake pads.

These findings are comparable to the study by Tomasévić *et al.* (2005). They detected Si, Al, C, Fe, Mg, S, Ca, K, and Cl in a biomonitoring study on metal particles deposited on some deciduous leave in urban area and concluded that the presence of these elements might suggest that the particles deposited on leaves mostly originated from traffic or re-suspended particulate matter. From the SEM/EDX analysis, Pb was not detected. There is every possibility that this is not unconnected to the ban on leaded petrol usage. Noble *et al*. (2004) carried out a biomonitoring study using ryegrass and other bioindicator plants

near a highway, and concluded that the non-detectability of Pb may be due to the phase-out of leaded petrol in Europe.

The morphology of the analysed particles was either spherical or smooth surfaces, a further indication that particles deposited on leaves mostly originated from the traffic, re-suspended particles, or local sources. However, Ca, Mg and Zn may have been dependent on selective uptake related to their preserved vitality during exposure (Tretiach *et al*., 2007). Despite traffic frequency differentials between the sampling sites, heavy metals, e.g. Cu and Mn, where found in abundance in ryegrass at Strefford, All Stretton and Craven Arms sites. These elements can penetrate the cuticles of plants and are readily absorbed (Radojević & Bashkin, 2006) so their accumulation can be described as an indication of heavy metal pollution.

5.10: Conclusion

Following the field and experimental analyses in this study, it is established that

- Both short-term and diffusion tube techniques are very useful in providing a good estimate of mean concentration exposures of gaseous pollutants over a relatively long sampling period.
- The spatial and temporal distributions of the main gaseous pollutants considered in this study followed traffic pattern and depicts traffic origin.
- Influence from meteorological parameters can contribute to the spatial and temporal distributions of gaseous pollutants.
- There were no results to show that hourly mean SO_2 exceeded the limit value of 350 $\mu g/m^3$ in the study area throughout the study period.

- Results show NO_2 exceedances of the set limit of 200 μg/m^3 at 5, 50 and up to 100 metres away from the trunk road depending on traffic frequency and driving scenarios.
- The vegetation samples collected at the four sampling sites indicated the presence of elements that can be associated to mainly traffic, such as erosion and deterioration of catalytic converters, vehicle engine, tyre wear, brake lining abrasion, constituents and additives of oil and petrol, and road dust re-suspension.
- The roadside presence of heavy metals was found in levels that are of different magnitudes higher than those at 50 and 100 m from the trunk road.
- Heavy metals exhibited trends that followed traffic pattern, showing high concentrations in locations of proximity to traffic presence.
- The study demonstrates that both plant species could be successfully applied in the determination of trends and pollution status of traffic-related heavy metals and are therefore suitable as bioindicators.

Chapter Six

Conclusion and Recommendations

6.0 Introduction

This chapter presents the overview of the findings of this study by reviewing the aims and objectives and stating the overall significance of the study. It also highlighted the study limitation and further areas of research proposed.

6.1 General overview

This study investigated rural air quality by monitoring monthly concentrations of nitrogen dioxide (NO_2), sulphur dioxide (SO_2), and hydrocarbon (HC) pollutants along the A49 trunk road carrying between 300 and 540 vehicles per hour. Measurements were carried out at four sampling sites in the order of 5 m, 50 m, and 100 m away from the road using different sampling techniques. The short-term sampling technique (Dräger tubes) did not detect SO_2 concentrations at all distances and sampling sites throughout the sampling period.

The application of the passive sampling technique measured concentrations of NO_2 and SO_2 over a three-weekly period every month using diffusion Dräger tubes. Sample collection was at 2 m above ground level, representing the breathing zone. Results show that mean concentrations of both pollutants correlated negatively with distance, having attained maximum levels at roadside measurements and declined with progressive distance from the road. This was similar to the short-term sampling technique and related with other air quality monitoring studies. Sulphur dioxide showed a time-weighted mean concentration that was below the set guidance limits at all distances and all four pairs of sampling sites throughout the study period. Spatial and temporal variations in NO_2 and

HC pollutant concentrations followed well-established patterns of distribution. Concentrations of both pollutants correlated negatively with distance, being that maximum roadside concentrations declined with increasing distances from the road. Results compared to other studies showed similar distance-decay trends in proximity to a major road. Statistical analyses suggest the influence of distance on the pollutants being significantly different between distances from the trunk road. Similarly, test for road traffic influence on concentration distributions of NO_2 and HC emissions showed positive correlation at all four sampling site pairs.

When compared with the national air quality standards and objectives for compliance, this study found mean concentrations for NO_2 above guidance level at 5 and 50 m and up to 100 m distances from the trunk road particularly at Church Stretton and Craven arms. This is an indication of traffic origin since both sampling sites were characterised by higher traffic frequency than All Stretton and Strefford sampling sites. It shows that inhabitants within this range of distance considered in this study are at risk of high exposure of NO_2 emissions. Contrasting trends were obtained for SO_2 levels at all distances as they were below the set limit, thereby suggesting that there are no immediate epidemiological concerns for inhabitants within the studied range of distance. Despite that the concentration levels of HC was high, this study did not establish any guidance limit for HC since they are not included in regulations at present. Statistical analyses between the pollutants from the first and second campaigns as well as between distances were significant.

Hazel leaf and ryegrass samples collected at four pairs of sites in rural South Shropshire, West Midlands at different distances (5, 50, and 100 m) from the A49 trunk road were analysed for the presence and pollution level of heavy metals. Results indicated no particular trend in elemental distribution but individual elements show higher concentrations in hazel leaf sample than ryegrass, thus suggesting that differences in leaf arrangement, morphology, surface characteristics and height of vegetation may have played considerable roles in the elemental profiling in both samples. The consequence of this is that breathing height exposure will potentially result in a significant immediate risk. Although elemental levels were generally low and inconsistent, heavy metals, such as Zn, Pb, Ti, Ni, Cu, Cr, predominantly exhibited high concentrations at roadside measurements and at locations with more traffic frequency. Thus, it is evident that the presence of heavy metal concentrations near road source will provide a good correlation with traffic indicators, offering further evidence that traffic remains a significant source of heavy metal pollution levels in vegetation. Statistically, results showed that distance had a significant influence over particulate deposition on ryegrass as well as hazel leaf samples. Emitted deposits contain elements that can be associated to vehicular traffic and this evidently signifies that heavy metals near roads are partly or wholly emitted from vehicle exhaust, erosion and deterioration of catalytic converters, tyre rubber wear, brake and tyre lining abrasions.

Other possible sources including root uptake from the soil, long-range transport, road dust re-suspensions and soil are inevitable. However, because the soils around the sampling locations predominantly consist of quartz grains in addition to the absence of any volcanic mineralisation in the catchment, the occurrence of elemental concentrations

in particulate deposits on leaf and grass surfaces collected in this research is an indication of traffic-related rather than geological sources.

6.2 Significance of the study

Air quality monitoring represents a significant method for the evaluation of current air pollution within the context of determining the risk of public exposure especially in areas with the likelihood of exceeding air quality objectives.

The findings of this study suggest that mean concentrations of NO_2 exceeded the NAQS set limits up to 100 m distance from the trunk road. Based on this, inhabitants in close proximity to roadways especially motorists, pedestrians and office workers are prone to potential exposure to high NO_2 that comes with its attendant epidemiological risks.

Although ryegrass and hazel leaves may not form part of the human diet, the findings have shown that plants can provide the potential pathway for air pollutants into food chain, resulting in exposures to health risks for consumers. Thus, this study can provide further information concerning environmental and human health monitoring for the local councils and other relevant agencies in dealing with air quality challenges.

6.3 Study strengths and limitations

Strengths: A distinctive strength associated to this study was the combination of monitoring techniques applied to investigate the concentrations of pollutants arising from major vehicular areas in rural environment. Each technique characteristically examined specific sample materials and the results obtained analysed independently with the aim of comparing between different techniques.

Another unique strength of this study was the duration of sampling. The study monitored rural air quality at four rural roads along A49 trunk road for the duration of 22 months spanning over three years. Continuous air sampling was carried out uninterruptedly at all four sites with the same procedures, ensuring that sampling errors were completely avoided or kept at the minimum in order that results of the spatial and temporal distribution were true representatives of traffic emissions. Quality control was maintained during the procedural biomonitoring samplings throughout the sampling season, ensuring that only intended vegetation samples were actually sampled. Reason for this was to avoid any result variability due to sampling errors. Overall, continuous sampling was conducted during relatively stable conditions throughout the sampling periods.

Limitations: This study only monitored air pollutants of interest and as such, its findings are only limited to the measured pollutants. This study therefore may not provide an all-inclusive conclusion for all exposures of public health interests. Another limitation is in the hourly traffic volume. Traffic volume was obtained by manual counting, hence the possibility of error resulting from either double or omitted counting especially during peak traffic flow in rush hours. Findings from this study apply to the hourly traffic volume similar or equivalent to the range obtained here as well as restricted to locations with similar site features.

In an attempt to compare traffic influence on the temporal and spatial distribution of gaseous pollutants, main metallic pollutants were also measured with respect to distance from the road by analysing vegetation samples at the respective sample locations as the air samples. This is because it is expected that at various distances from the road,

particulate deposits will vary. Though the uncertainty of the source and how much various deposit rates will influence the elemental components of the studied plants over a period of time would require that elemental analysis of soils from each location be performed, this was not captured within the scope of this study since it was mainly for the purpose of comparing with results from gaseous pollutants from air sampling device.

6.4 Recommendations for further studies

Notwithstanding the primary objectives of this study were accomplished, it is not clear if the applications of these findings may be restricted to locations with similar background and characteristics. Further study is therefore required for different road types and traffic conditions.

Although hazel leave and ryegrass are potential suitable biomonitors, it is a known fact that various species and tissues of plant samples have different assimilation tendencies for different elements. Therefore, it will be interesting to monitor air pollution in a similar rural setting with different plant species, as well as different plant tissue to carry out similar study. Because this work had not performed elemental analysis of soils from each location for comparison purposes, future work should incorporate the chemical analysis of the road dust or soil samples collected at the studied sampled locations.

Similarly, the sampled locations were quite further apart and the sampling transects restricted to 100 m from the trunk road. Further study with locations of closer proximity and an extended distance beyond 100 m is also recommended.

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Appendix

Appendix 1: Meteorological conditions of sampling sites between June 2008 and April 2010.

Note: W/S = wind speed; Temp = Temperature; R/H = Relative humidity; LD = Lost data.

	All Stretton			Strefford			Church Stretton			Craven Arms		
Month	**W/S (m/s)**	**Temp (°C)**	**R/H (%)**	**W/S (m/s)**	**Temp (°C)**	**R/H (%)**	**W/S (m/s)**	**Temp (°C)**	**R/H (%)**	**W/S (m/s)**	**Temp (°C)**	**R/H (%)**
17 Jun, 08	2.4	14	43	0.5	14	43	2.3	16	42	2.2	15	48
Jul 8	2.8	15	46	1.5	13	47	2.9	14	43	2.4	17	41
Aug 15	1.9	16	48	1.8	15	46	2.0	15	50	1.7	16	55
Sep 19	2.6	13	44	2.0	12	45	2.2	14	45	2.3	14	51
Oct 14	1.4	12	49	2.1	13	46	1.3	13	45	1.4	12	46
Nov 25	2.2	11	52	2.5	15	51	1.9	14	53	2.0	15	55
Dec 11	1.3	11	61	1.3	10	63	1.1	11	62	1.2	11	60
22 Jan, 09	0.5	09	66	0.6	08	62	0.5	08	64	0.4	08	67
Feb 18	0.7	08	58	0.5	07	55	0.6	08	53	0.7	08	55
Mar 12	1.9	12	50	1.7	12	48	2.0	13	49	1.9	12	51
Apr 01	2.1	14	49	1	13	50	1.8	15	48	0.9	15	50
May 07	1.8	15	48	1.9	15	49	1.7	15	47	1.8	17	49
Jun 18	3.1	16	53	2.9	16	52	3.0	16	55	2.8	16	50
Jul 15	2.0	16	50	1.3	15	50	1.9	15	51	1.9	17	49
Aug 20	2.3	17	51	3.0	17	55	2.7	18	52	3.0	18	49
Sep 29	1.9	15	47	1.8	16	48	LD	LD	LD	LD	LD	LD
Oct 20	2.1	13	43	1.2	14	43	LD	LD	LD	LD	LD	LD
Nov 26	2.9	10	52	2.8	11	49	LD	LD	LD	LD	LD	LD
Dec 17	1.7	10	63	1.4	10	62	LD	LD	LD	LD	LD	LD
15 Jan 10	0.6	07	69	0.5	07	61	LD	LD	LD	LD	LD	LD
Mar 26	2.3	12	52	2.0	12	50	LD	LD	LD	LD	LD	LD
Apr 06	2.5	14	48	2.1	13	49	LD	LD	LD	LD	LD	LD

Appendix 2: Hourly traffic counts along the selected sites of A49 trunk road. Numbers in bold represent subtotal and total traffic frequencies

	All Stretton				Strefford				Church Stretton				Craven Arms			
Month	**HGV**	**LGV**	**CAR**	**Sub Total**	**HGV**	**LGV**	**CAR**	**Sub Total**	**HGV**	**LGV**	**CAR**	**Sub Total**	**HGV**	**LGV**	**CAR**	**Sub Total**
17 Jun, 08	24	52	224	**300**	28	36	276	**340**	56	84	368	**508**	48	100	392	**540**
Jul 8	28	32	184	**244**	28	32	212	**272**	60	96	328	**484**	64	104	348	**516**
Aug 15	24	32	168	**224**	32	48	204	**284**	56	104	412	**572**	72	116	340	**528**
Sep 19	32	36	248	**316**	40	52	208	**300**	52	116	324	**492**	76	108	412	**596**
Oct 14	28	32	240	**300**	32	56	248	**336**	64	108	316	**488**	72	112	336	**520**
Nov 25	36	44	200	**280**	28	36	212	**276**	64	104	328	**496**	60	108	332	**500**
Dec 11	28	40	312	**380**	36	60	232	**328**	60	100	332	**492**	68	104	456	**508**
22 Jan, 09	44	48	204	**296**	24	36	220	**280**	68	96	328	**492**	76	116	392	**584**
Feb 18	40	72	116	**228**	28	32	216	**276**	44	92	368	**504**	64	112	412	**588**
Mar 12	48	64	196	**308**	40	68	128	**236**	64	100	312	**476**	72	104	348	**524**
Apr 01	28	52	204	**284**	24	36	232	**292**	68	112	316	**496**	72	116	440	**628**
May 07	48	56	264	**368**	32	40	200	**272**	56	104	312	**472**	60	108	396	**564**
Jun 18	44	48	216	**308**	28	60	212	**300**	48	100	372	**520**	64	112	388	**564**
Jul 15	36	48	176	**260**	36	56	228	**320**	56	108	328	**492**	52	104	372	**528**
Aug 20	44	76	200	**320**	54	76	188	**318**	52	96	332	**480**	68	112	336	**636**
Sep 29	28	40	212	**280**	32	60	196	**288**	60	104	368	**532**	56	116	436	**608**
Oct 20	36	40	276	**376**	40	64	240	**344**	56	92	376	**524**	60	100	376	**536**
Nov 26	40	52	208	**300**	44	56	204	**304**	48	96	412	**556**	56	108	388	**552**
Dec 17	40	56	316	**412**	36	48	336	**420**	64	112	428	**604**	64	96	496	**656**
15 Jan, 10	48	44	280	**404**	28	48	256	**332**	56	108	336	**500**	72	100	304	**476**
Mar 26	44	72	220	**336**	54	56	244	**354**	64	112	296	**472**	68	112	396	**576**
Apr 06	52	64	276	**392**	32	64	292	**388**	52	104	300	**456**	64	96	312	**472**
Total	**848**	**1104**	**4940**	**6892**	**756**	**1120**	**4984**	**6860**	**1268**	**2248**	**7592**	**11108**	**1428**	**2364**	**8408**	**12200**

Appendix 3: Hourly traffic flows on A49 southbound between B4361 and A4103 (E350212, N245003) between Thursday 1st Jan 2009 and Thursday 31st Dec 2009).

	Mon	Tue	Wed	Thur	Fri	Sat	Sun	Mn-Fr	Mn-Sn
	x36	**x37**	**x37**	**x38**	**x37**	**x37**	**x36**	**Mean**	**Mean**
01:00	19	21	22	24	24	40	48	22	28
02:00	15	14	16	17	18	26	34	16	20
03:00	14	11	14	14	15	23	26	13	16
04:00	16	16	15	18	16	21	22	16	17
05:00	27	28	26	25	27	17	12	26	23
06:00	87	84	82	81	78	48	25	82	69
07:00	170	175	181	166	163	75	49	171	139
08:00	537	568	580	550	513	160	80	549	426
09:00	588	631	636	606	574	306	132	607	496
10:00	486	532	555	523	512	466	285	521	479
11:00	491	493	502	490	491	567	447	493	497
12:00	497	489	496	490	529	619	514	500	519
13:00	495	484	491	482	534	589	532	497	515
14:00	506	496	498	491	548	555	469	507	509
15:00	510	497	515	509	589	525	452	524	513
16:00	519	532	531	550	617	487	433	549	524
17:00	519	536	549	548	567	430	416	543	509
18:00	570	609	620	602	573	373	373	594	531
19:00	369	414	434	434	456	322	342	421	395
20:00	252	283	295	296	360	259	267	297	287
21:00	158	172	182	198	229	169	183	187	184
22:00	114	126	130	148	153	121	124	134	130
23:00	78	93	96	97	112	89	69	95	90
24:00:00	40	43	45	47	67	72	40	48	50

Appendix 4: List of Publications

Validating the correlation of traffic-associated hydrocarbon and nitrogen dioxide with distance from a trunk road within a rural environment in UK. *Microchemical Journal* **99** (2011), 138-144.

Influence of vehicular traffic on a major trunk road on rural air quality in UK. *Microchemical Journal* **99** (2011), 344-351.